Mortalities of Juvenile Atlantic Salmon Caused by the Fungicide OBPA

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MORTALITIES OF JUVENILE ATLANTIC SALMON CAUSED BY THE FUNGICIDE OBPA

by

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ABSTRACT

Zitko, V., L. E. Burridge, M. Woodside, and V. Jerome. 1985. Mortalities of juvenile Atlantic salmon caused by the fungicide OBPA. Can. Tech. Rep. Fish. Aquat. Sci. 1358: iii + 26 p.

The most probable cause of the mortalities is the fungicide OBPA, 10,10'-oxybis-10H-phenoxarsine, present in a plastic liner of the fish tanks. Such a liner must not be used in aquaculture systems based on water recirculation and we do not recommend its presence even in flow-through systems since chronic effects of OBPA are unknown and OBPA is not registered for this application. Results of the analyses of fish, fish food, and plastic liners for heavy metals and organic chemicals are described.

RÉSUMÉ

Zitko, V., L. E. Burridge, M. Woodside, and V. Jerome. 1985. Mortalities of juvenile Atlantic salmon caused by the fungicide OBPA. Can. Tech. Rep. Fish. Aquat. Sci. 1358: iii + 26 p.

Selon toute probabilité, la cause des mortalités est le fongicide OBPA, 10,10'-oxybis-10H-phénoxarsine, présent dans la doublure de plastique des bassins contenant les poissons. Une telle doublure ne peut être utilisée dans des systèmes d'élevage où l'eau est recirculée, et nous ne la recommandons pas même dans des systèmes à débit continu, car les effets chroniques de l'OBPA ne sont pas connus et cette substance n'est pas enregistrée à cette fin. Nous présentons les résultats de dosages de métaux lourds et de substances chimiques organiques chez les poissons, dans les nourritures à poissons et dans les doublures de plastique.

INTRODUCTION

In early September 1984, Strang's Salmonid Hatchery, Penobsquis, N. B., encountered extensive mortalities of juvenile Atlantic salmon (Salmo salar). The mortalities occurred a few days after the fish were moved into tanks equipped with a new plastic liner. Over the period of about 2 wk, approximately 58,000 juvenile Atlantic salmon died. Water samples were analyzed by two laboratories and no problems were obvious: chlorine (Cl), arsenic (As), cadmium (Cd), and copper (Cu) were not detectable at 0.005, 0.05, 0.01, and 0.01 mg/L, respectively, and zinc (Zn) was present at 0.015 mg/L.

No diseases were detected by the Department of Fisheries and Oceans (DFO) Disease & Nutrition Section; however, the body surface of the fish was unusually free of bacteria. Materials used in the hatchery were considered next. The most obvious suspect was the plastic liner. A visual inspection identified it tentatively as plasticized polyvinyl chloride (PVC), probably containing a germicide to protect the plasticizer. A few inquiries established that the germicide is OBPA.

OBPA is registered in Canada as a fungistatic additive to 10-12 commercial products such as swimming pool liners and shower curtains, and carries the standard "toxicity to fish & wildlife" label (Dr. A. Carter, Agriculture Canada, Ottawa). According to Morton Thiokol Inc., "VINYZENE(R) antimicrobials are toxic to fish and wildlife. "VINYZENE(R) should not be discharged where it will drain into lakes, streams, ponds, or public water." (see, Morton Thiokol Inc., Ventron Division. VINYZENE(R) ANTIMICROBIALS. 425-083; MATERIAL SAFETY DATA SHEET 425-024). According to the manufacturer, the solubility of OBPA in water is 5 mg/L. The LC50 of OBPA to bluegill is 14, 12, and 8 ug/L at 24, 48, and 96 h, respectively. The usual application rate of OBPA in plastics is 500 mg/kg.

MATERIALS

FISH AND FISH FOOD

Five samples of dead fish were received from Strang's Hatchery. Four originated from individual tanks, the fifth contained a mixture of dead fish from all tanks. A sample of fish food was also obtained. Weight and length of analyzed fish were 5.17 g (S.D. 1.6, n=16), and 8.0 cm (S.D. 0.76, n=7), respectively.

LINER

Four samples of a blue, "thick" liner were obtained from Strang's Salmonid Hatchery. Another two samples were obtained from Louis White, Sr., Atlantic Smolts Ltd. A sample of a "thin" liner used in Strang's Hatchery in some tanks was also obtained.

Strang's Hatchery purchased the liner from Scarborough Canvas Ltd. (Mr. R. MacKinnon) and, according to Mr. Strang, he was not told about the unsuitability of the liner for hatchery use. Mr. MacKinnon was contacted by us and identified the liner as a PVC swimming pool liner, not recommended for hatchery use. The liner is manufactured in Canada by Canadian General Tower Ltd., 52 Middleton Street, Cambridge, Ontario, N1R 5T6 (Gary Lloyd).

Mr. Lloyd confirmed that the liner is not for hatchery use. For this purpose they have a food-grade liner under development. Our questions about additives in the liner were answered by Mr. Solly Gagnon, Canadian General Tower Ltd., who disclosed the presence of OBPA, heat stabilizers (cadmium, barium and sometimes zinc complexes) added as a proprietary liquid, and plasticizers (phthalates and epoxidized soybean oil). Titanium dioxide is used as a filler and the blue dye is phthalocyan blue.

OBPA

OBPA (10,10'-oxybis-10H-phenoxarsine, C24.H16.As2.O3, RN 58-36-6) is manufactured by Morton Thiokol/Ventron Division Chemicals Division, 150 Andover Street, Danvers, MA 01923.

OBPA is available commercially under the tradename VINYZENE(R) as a 2% solution of OBPA in a plasticizer (epoxidized soybean oil, diisodecyl, di(2-ethylhexyl), or butylbenzyl phthalate), in polydiethylene adipate or in polypropylene glycol. A sample of VINYZENE(R) BP-5-2DIDP Lot 27741 was obtained from the manufacturer. Another sample (VINYZENE(R) BP-5-2DOP) was obtained from Canadian General Tower Ltd.

METHODS

ANALYSES FOR INORGANICS

Samples of fish, liner, and water from toxicity testing were analyzed for Cu, Cd, Zn, and lead (Pb) by atomic absorption spectrophotometry (AAS). Samples of VINYZENE(R), liner, and water from toxicity testing were analyzed for As by AAS. Cd was also determined in VINYZENE(R).

Whole fish (wet weight 3.9 to 11.1 g) from Strang's hatchery were rinsed, freeze-dried, and crushed. Subsamples (0.35 g) were ashed for 16 h at 450°C, dissolved in 0.5 mL concentrated nitric acid (Aristar grade, B.D.H., Poole, England) and made to volume in deionized water. Results are expressed on a dry weight basis. Samples of liner were ashed and dissolved in nitric acid for all metals except As. As was determined in ethyl alcohol extracts of liners as suggested by Morton Thiokol Inc. Water samples were acidified with nitric acid (0.5 mL 10% per 30 mL sample) and analyzed directly. VINYZENE(R) was dissolved and diluted in ethyl alcohol.

Cd and Pb standards for graphite furnace were dilutions of a stock matrix containing Cu, Cd, Cu, Fe, Mn, Pb, and Zn (50, 0.5, 20, 200, 50, 5, and 20 ppm, respectively). Cu and Zn standards for flame were dilutions of 980 mg/L Cu(NO3)2 and 1000 mg/L Zn(NO3)2 standard solutions, respectively. All furnace standards contained 1% HNO3. Accuracy was confirmed against NBS oyster tissue (SRM#1566) and NBS water (SRM#1643a). The As value was high, 107 µg/L, compared to the NBS water value of 76+7 µg/L when an external standard was used. Standard addition method yielded the value of 72.6 µg/L. Standards of As for flame AAS were made from the sodium salt of dimethylarsinic acid (Na(CH3)2AsO2) dissolved in ethanol.

Table 1. Atomic absorption spectrophotometry conditions.

	Cd	Pb	As
	Furnace		
Lamp-Type	EDL#7815	EDL#8859	EDL#8515
λ(nm)	228.3	283	197.3
Power	5w	10w	8w
Background Correction	Y	Y	Y
Slit	4	4	4
Method	curve	curve	std addn
Low std ng/g	0.50	5.0	25
High std ng/g	6.25	62.5	100
Analyzed-			
Water	Y	Y	Y
Liner	Y	Y	
Fish	Y	Y	
VINYZENE(R)	Y		
Food	Y	Y	
Purge Gas	N2	N2	N2
Recorder Range mV 10	5	5	
Program-			
Dry °C	130 30	130 30	130 30
Char	300 10	650 10	300 18
Atomize	2100 5	2200 6	2700 8
Clean	2550 3	2550 3	2550 5

Note: Dry and char times were lengthened when injection volume <30 µL and when sample contained ethyl alcohol.

	As	Cu	Zn
	Flame		
Lamp-Type	EDL#8515	HCL#215856	EDL#1942
-λ(nm)	197.3	325	214
-Power	8w	15mA	6w
Background Correction	Y	Y	Y
Slit	0.7nm HIGH	0.7nm HIGH	0.7nm HIGH
Method	curve or std addn	curve	curve
Low std µg/g	6.2	0.05	0.05
High std µg/g	49.6	1.00	0.50
Analyzed-			
Water		Y	Y
Liner	Y	Y	Y
Fish		Y	Y
VINYZENE(R)	Y		
Food		Y	Y
Fuel (C_2H_2)			
Pressure psi	12	12	12
Flow Setting	16	24	24
Oxidant(AIR)			
Pressure psi	52	52	52
Flow Setting	37	40	40
Zeroed on	ethyl alcohol	water	water
Absorbance	0.10/0.10	0.22/0.22	0.10/0.12
Using µg/g	20	5	0.5
Settings for all	CONC,HOLD,REC ABS,3 AVG,t = 1 sec		

Note: Absorbance read on settings ABS,CONT(no 3 AVG).

Graphite furnace analysis was performed on a Perkin-Elmer 503 AAS with HGA-2100 controller, HGA ramp and deuterium arc background correction. A Perkin-Elmer 5000 AAS was used for flame analysis. All lamps were electrodeless discharge except the hollow cathode Cu lamp. Instrument conditions are in Table 1.

ANALYSES FOR ORGANICS

Fish and a food were homogenized by grinding with sodium sulfate extracted with hexane as described by Zitko et al. (1974). The extracts were analyzed by gas chromatography on a Varian model 3700 gas chromatograph equipped with a Ni63 Electron Capture Detector. A 6-m column packed with 3% OV-101 was used and temperatures maintained as follows: column 180°C; detector 300°C; injector 210°C.

A Finnigan 9610 Gas Chromatograph equipped with a fused silica SE54-30N capillary column, about 30 m, and a J & W on-column injector, were used to analyze extracts of VINYZENE(R), liner, hatchery fish, and fish food. The column was at 80°C for 0.5 min, then the temperature was increased to 250°C at 5°C/min and held for 20-40 min. Helium was the carrier gas.

The capillary column was inserted into the ion source of a Finnigan model 4500 mass spectrometer. The operating conditions of the mass spectrometer were: emission current 300 mA, electron multiplier -1200 V, quadrupole offset -8.7 V, and the pre-amplifier sensitivity was 1E-7 or 1E-8 as required. The perfluorotributylamine calibration achieved with the following parameters (typical values) Accl = Acc2 = 0, Extractor = -18 V, Lens = -143 V, and Quad Ent = -18.1 V was usually within 6 mmu.

Electron impact (EI) and methane chemical ionization spectra (CI) were obtained, the latter in the PPINICI mode (Pulsed Positive Ions and Negative Ions Chemical Ionization), yielding PICI and NICI, Positive and Negative Ions Chemical Ionization spectra, respectively.

OBPA

Two methods for the determination of OBPA were obtained from Morton Thiokol Inc. (A. L. Norris, Jr.). Unfortunately, the methods (M&S #003 and 008) arrived only after the completion of the investigations. Method M&S #003 deals with the determination of OBPA in VINYZENE(R) products or plasticizers. These are dissolved in ethanol and analyzed by flame AAS. A certified VINYZENE(R) is used for calibration. Method M&S #008 describes the determination of VINYZENE(R) in vinyl films and is based on acid digestion of organic material.

We used Soxhlet extraction with ethanol instead. Dimethylarsinic acid or its sodium salt, or VINYZENE(R) BP-5-2DIDP lot #27741 (certified OBPA content 1.99%) were the standards. Arsenic in VINYZENE(R) and in ethanol extracts of the liners was determined by flame AAS. Even small amounts of solvents other than ethanol interfered with the determination. Graphite furnace AAS was used to determine As in water samples from toxicity tests. The presence of 1% nitric acid is required for stable and reproducible results and good sensitivity.

In an attempt to isolate the fungicide OBPA, 20 mL of VINYZENE(R) BP-5-2DOP was extracted with 250 mL of a 30% (v/v) aqueous ethanol followed by 100 mL of chloroform. The chloroform extract was made up in 10 mL ethanol after the removal of chloroform. In another attempt VINYZENE(R) BP-5-2DOP (11.3 g in hexane) was loaded on a column containing a mixture of 25 g granulated charcoal and 10 g of decolorizing carbon. The column was eluted with 110 mL hexane, 85 mL chloroform, and 95 mL benzene. The solvents were removed by using a rotary evaporator. Aliquots of the residues (0.1 mL or the whole residue, if < 0.1 mL) were dissolved in ethanol. The charcoal from the column was slurried with chloroform, benzene, and acetone, respectively. Each fraction was filtered, and processed as above. All fractions were analyzed by GCMS and AAS.

Liner Extraction

A sample (2.5 g) of the liner was extracted by refluxing with diethyl ether yielding 0.9 g of extract. The extracted liner was macerated with chloroform resulting in an additional 0.23 g of material. Another sample (4.5 g) was extracted twice with boiling water and then with diethyl ether in a Soxhlet, yielding 1.5 g of extract and 3 g of residue. UV and fluorescence spectra of the aqueous extracts were obtained, the extracts were analyzed by AAS for Cd, and extracted with hexane and with diethyl ether at pH=2. The hexane and ether extracts were analyzed by gas chromatography-mass spectrometry (GCMS).

Soxhlet extraction of liner sample #2 with ether yielded 1.84 g of extract. This extract was used in most toxicity tests. Samples of Strang's and White's liners were extracted with ethyl alcohol in a Soxhlet for up to 24 h for OBPA determination and toxicity tests.

To identify the polymer in the liners, samples of liners were dissolved by prolonged refluxing in dichloromethane (about 12 h, 0.5 g liner/300 mL). A few remaining particles were filtered off on glass wool, the filtrate was concentrated to about 100 mL on a rotatory evaporator and poured into 500 mL of absolute ethanol. The precipitated polymer was centrifuged, washed with ethanol, dried on a rotary evaporator and its IR spectrum was determined. The supernatant from the centrifugation was evaporated to dryness on the rotary evaporator yielding 70 and 270 mg of a residue from the "thin" and "thick" liners, respectively. The residues were oily and contained some particles. The oils were dissolved in hexane, the particles were filtered off (glass wool) and the solutions were analyzed by GCMS.

IR, UV, and Fluorescence Spectra

Infrared spectra (IR) of liner extracts, polymer and of VINYZENE(R) were obtained on the Perkin-Elmer model 700 IR spectrophotometer. Spectra of the extracts were measured undiluted, those of the polymers were measured in potassium bromide disks. Fluorescence spectra were recorded on a Perkin-Elmer model MPF2A spectrofluorometer. A Beckman model 25 UV/VIS spectrophotometer was used to monitor the leaching of organic compounds from the liner by water.

TOXICITY TESTING

Static toxicity tests were carried out at water temperatures of 9-11°C. Atlantic salmon (0+) ranged in size from 4.7-10 cm (mean = 7.7; S.D. = 0.5) and from 0.7-8.4 g (mean = 4.5; S.D. = 1.0). Over 70% of the test animals were males.

Toxicity of Liner

A piece of the liner (11 g) was placed in a 4-L Erlenmeyer flask containing 3 L of water and three fish. Tests with ether and ethanol extracts of the liner were performed similarly. Nominal concentrations of the extracts were 2-17 and 20-153 mg/L, respectively. Control tests accompanied all toxicity tests.

Toxicity of Cd Stearate and OBPA

Two components of the liner were identified and tested for toxicity to salmon. Cd was assumed to be present as Cd stearate and a preparation SU-266 from the Chem Service surfactant kit (Chem Service, Media PA.) was used. Two formulations of the fungicide as well as a preparation with OBPA removed were tested. Cd stearate was melted on Ottawa sand and the contaminated sand placed in the flasks. Water samples were taken at 0, 3, 6, 12, 24, 48, 72 and 96 h. The nominal coucentration of Cd ranged from 0.03-0.23 g/L as Cd stearate.

The toxicity of VINYZENE(R) BP-5-2DIDP was initially tested by adding the undiluted preparation to the 4-L flasks. The VINYZENE(R) proved so toxic that VINYZENE(R) was dissolved in ethanol and aliquots were applied to the bottom of the 4-L flasks. Test concentrations (nominal) ranged from 0.2-5 mg/L as VINYZENE(R).

Uptake of Elemental Sulfur from Food

When elemental sulfur was identified in the food and fish, its fate and effects on juvenile Atlantic salmon were studied in a brief feeding experiment with 28 fish fed Purina Trout Chow (from Strang's Hatchery) for 1 wk. The fish ranged in length from 5.0-6.6 cm (mean = 5.9; S.D. = 0.5) and in weight from 1.1-2.7 g (mean = 1.8; S.D. = 0.4). Four fish were taken at t = 0, 7, 24, 48, 72, 96 and 168 h. The digestive tract was removed from two fish from each sample and one dissected and one non-dissected fish were analyzed as described (Zitko et al. 1974).

RESULTS AND DISCUSSION

METALS

The "thick" and "thin" liners are 0.74 and 0.21 mm thick, and weigh 0.11 and 0.0219 g/cm^2, respectively. White particles of TiO2 remain after ashing and they do not dissolve in nitric acid. The concentrations of Cu, Cd, Zn, and Pb appear within the normal range for fish as well as for fish food (Table 2). Such levels are not associated with acute or chronic effects. The "thick" liner contains Cd in a fairly high concentration, with little variation between samples (347, 389, 430, and 420 µg/g for #1-#4, respectively). The concentration of Cd in Strang's "thin" liner is much lower (0.93 µg/g) in comparison.

The extent of leaching of the metals by water was determined by partially submerging 14 sq cm of new liner in 1 L soft tap water (hardness 14 mg/L). In 2 d, metal levels rose from nondetectable to 140, 50, 4.5, and 1 µg/L, for Cu, Zn, Cd, and Pb, respectively. On the tenth day the levels of Cd and As were 12.5 and 514 µg/L.

OBPA

According to the manufacturer, the concentration of OBPA in the liner is about 149 µg/g, expressed as As, with a usual range of 100-167. The concentration of OBPA in Strang's liners #1-#4 and in White's liner was 91, 78, 77, 72, and 69 µg/g as As, respectively. These concentrations are 53% (Strang) and 46% (White) of the nominal value. It is not known whether the lower-than-nominal concentrations are accurate or are caused by a bias in the method used. It appears that White's liner contains less OBPA than Strang's liners #1-#3.

VINYZENE(R) contains 2% OBPA (5970 µg/g As). Values of 4770, 4870, and 5280 µg/g were determined experimentally. The average (4970 µg/g S.D.270) equals 83.2% recovery. The reasons for the relatively low recovery were not investigated. VINYZENE(R) contained only traces of Cd (0.47 ng/g).

The major component of VINYZENE(R) BP-5-2DOP was confirmed as di(2-ethylhexyl)phthalate (DEHP). The PICI spectrum (Fig. 1) shows the [molecular+1] (M+1) ion at 391 m/z and major ions at 113, 149, and 279 m/z. The base ion of the negative ion CI mass spectrum is at 148 m/z (not shown). VINYZENE(R) (BP-5-2DIDP) contains both DEHP and diisodecyl phthalates, the latter appearing as a number of peaks after scan 1200 (Fig. 2). Alcohols (Fig. 3), possibly dimethyl octanol and others, were found in both VINYZENE(R) samples.

OBPA is detectable in VINYZENE(R) after the preconcentrations described above. The base ion of OBPA is at 243 m/z (C12.H8.AsO+); an additional prominent ion is at 168 m/z (C12.H8.O+) and a relatively weak molecular ion is present at m/z 502. Pentyl benzoate (Fig. 4) was found in the concentrate. However, some pentyl benzoate was present also in the blank. OBPA was retained by the charcoal column as As was not detectable in the eluents by AAS. DEHP and various alcohols were found in all fractions. Some of the compounds in the first fraction originated from the carbon. Chloroform and benzene extracted OBPA from the charcoal, but the recoveries were not quantitative. OBPA was not extractable by acetone.

LINER

According to IR spectra, the polymer in the "thin" liner is PVC (Zeller and Pattacini 1973). The polymer in the "thick" liner appears to contain some polyvinyl acetate as well (fairly strong absorbance maximum at 1720 cm^{-1}). In each of the "thick" liner extracts the major components are five phthalates (Fig. 5). These were identified in the ether extract by using chemical ionization (Fig. 6-10). The phthalate in scan 336 (Fig. 8) has the same molecular ion and the same retention time as DEHP, but its mass spectrum suggests the presence of a C8 group other than 2-ethylhexyl. The phthalate #270 (Fig. 6) has a [M+1] ion at 335 m/z and an intense ion at 233 m/z, indicating a phthalate with two 6-carbon groups. The next peak (Fig. 7) has a

Table 2. Selected metals in fish, liner, food and toxicity tests (Mean, [S.D.], >Range<).

	Fish	Liner	Food	Water from liner #2 toxicity test (47 h)
Samples	10	2	2	1
Cu µg/g	2.94 [0.49] >2.25-3.82<	73.6 [2.3] >72.0-75.2<	16.8 [0.1] >16.7-16.8<	<0.05
Samples		9		2
Cd ng/g	113 [96.2] >33.6-327<	µg/g 391 [60.8] >313-518<	ng/g 529 [232] >365-693<	ng/g 0.92 [0.71] >0.42-1.42<
Samples		3		
Zn µg/g	147 [36.8] >91.8-203<	57.4 [2.1] >55.7-59.7<	235 [20] >221-249<	<0.05
Pb ng/g	422 [223] >237-941<	1540 [283] >1340-1740<	830 [79] >774-886<	<5
Samples As µg/g Strang's Hatchery	–	4 79.6 [8.4] >71.5-91.4<	–	0.029
Samples White's Hatchery		2 68.8 [3.4] >66.4-71.2<		

[M+1] ion at 363 m/z and ions and probably another [M+1] ion at m/z=391 and contains a mixture of diheptyl- and dioctyl-phthalate. The phthalate #392 (Fig. 9) has a [M+1] ion at m/z=419 and is a dinonyl phthalate. The final phthalate (#477, Fig. 10) has a [M+1] ion at 447 m/z and a major ion at 289 m/z, indicating two 10-carbon groups, but it is not the diisodecyl phthalate of VINYZENE(R) BP-5-2DIDP.

The liner also contains nonylphenol (Fig. 11, 12). Nonylphenol is very toxic to fish (McLeese et al. 1981), but in this case was probably only a minor factor contributing to the toxicity of the liner.

The "thin" liner contains DEHP and only traces of other phthalates.

UV spectra indicated considerable leaching of organic compounds from the "thick" liner into tap water. The leachate obtained by boiling (Fig. 13) contains phenol (scan 79), 2-ethylhexanoic acid (167), benzoic acid (203), nona-(245), deca-(311), undeca-(403), dodeca-(453), tetradeca-(588), and hexadeca-(716) -noic acid. Phenol,4,4'-(1-methylethylidene)bis-, (p,p'-Bisphenol A) is probably present in scan 840. A similar compound is in scan 760, and scan 406 may also contain a phenol.

FISH FOOD

The usual organochlorine contaminants (PCB, HCB, DDE, and nonachlor were not detectable in an injection equivalent to 25 µg lipid. The main components of the extract (Fig. 14) are squalene (scan 1208), ethyl esters of deca-, dodeca-, tetradeca-, hexadeca-, and octadexahexanoic acid, respectively (scans 325, 469, 604, 729, and 845), and methyl ester of hexadecanoic acid (688). Other minor peaks are mostly paraffins; the peak 471 is hexadecane, that in scan 541 is heptadecane, followed by pristane (2,5,10,14-tetramethylpentadecane in scan 545). Cycloparaffins or monounsaturated olefins are also present as minor peaks (655, 716, 830, 873). DEHP is present in scan 1030, but this may be an artifact due to laboratory contamination. Elemental sulfur is present in scan 744.

FISH

The main component of the hexane extract of fish is squalene (Fig. 15, scan 1217). Hexadecane (475) and pristane (548) are also quite prominent. Most of the other peaks (732, 795, 858, 906, 958, 1008, 1061, 1117, 1192, 1284, 1403, 1536, and 1753) are paraffins. Dibutyl phthalate (715) and DEHP (1034) are fairly low and may be due to contamination in the laboratory. Elemental sulfur is readily visible in scan 750. The "unresolved envelope" between scans 600 and 1000 appears to be due to cycloparaffins, among others. An unidentified compound is present in scan 1100 (Fig. 16). Fatty acid esters found in the food are not detectable. The usual organochlorine compounds (PCB, DDE, nonachlor) are not detectable in this EI run or in the subsequent NICI analysis. Hexachlorobenzene was readily detectable by the latter (Fig. 17). The response of elemental sulfur is also very strong in this mode. Spectrum of the EI unidentified compound (1100) in the PICI mode (Fig. 18) indicates that m/z=346 is the molecular ion. The compound yields a prominent [M+1]+ ion under the PICI conditions.

A comparison of the EI (Fig. 15) with the PICI (Fig. 19) chromatogram indicates an enhanced response of elemental sulfur (226) and of the "unknown" (332), as well as that of the "unresolved envelope" in the latter and underlines the advantage of using several ionization modes. PICI is also the method of choice for the determination of the molecular weight of paraffins, yielding very intense

$[M-1]^+$ ions. Thus the series of paraffins present in this sample ranges from C20 (222) to C30 (424).

Except for the uncertainty about the "unknown" compound, the analysis did not detect any chemicals acutely toxic to fish in realistic concentrations, either in the food or in the fish.

TOXICITY OF LINER

When 11 g of tank liner #1 were placed in 3 L of water with juvenile salmon, all fish died within 48 h. The ether extract of an equivalent amount of tank liner was not toxic to salmon in nominal concentrations up to 17 mg/L. The ethanol extract of the liner was toxic to the fish with an LC50 of 54 mg/L (nominal concentration). Liner #1 was more toxic than liners #2-4. This is probably the result of somewhat lower concentration of OBPA in the latter (see As concentrations given earlier).

Two components of the liner were also tested for their toxicity to Atlantic salmon. These were Cd stearate and VINYZENE(R) BP-5-2DIDP. The Cd stearate was not toxic to the fish. Water analysis indicated that Cd was present in high concentrations (0.3-1.9 mg/L) but there were no mortalities. Consequently, Cd in the form of Cd stearate is not available to the fish. On the other hand, VINYZENE(R) is highly toxic to juvenile Atlantic salmon (nominal 96 h LC50 = 2.86 mg/L).

The isolation of OBPA from VINYZENE(R) produced "OBPA-free" VINYZENE(R) fractions. Their toxicity was investigated as well to determine whether OBPA is the only highly toxic component of VINYZENE(R) (DIDP is not acutely toxic). Fractions 1-6 were pooled and the toxicity of this sample determined. There were no deaths of any fish during the 96-h test. The nominal concentration was 90 mg/L. In 96 h LC50 expressed as As is 15 µg/L, in good agreement with the values reported by the manufacturer. Additional details on the toxicity tests are given in the Appendix.

SULFUR IN FISH FOOD

The level of sulfur found in the fish food was 1.65 µg/g lipid weight. The concentration of sulfur found in the fish from Strang's Hatchery was 0.58 µg/g lipid weight.

The results of the feeding experiment are listed in Table 3. There were no mortalities. Some elemental sulfur was present at the beginning of the experiment in fish reared on uncontaminated food.

Table 3. Concentration of sulfur in fish fed sulfur-contaminated fish food for 1 wk.

Time h	Concentration (µg/g lipid)	
	Dissected fish	Non-dissected fish
0	0.41	0.18
7	0.02	>Contaminated sample<
24	0.66	0.70
48	0.52	0.64
72	0.50	0.66
96	3.34	0.54
168	0.22	0.32

There was only a slight increase in sulfur concentration in fish fed sulfur-contaminated food. The difference in sulfur concentration between dissected and non-dissected fish is minimal, indicating that sulfur is present in the digestive tract and in other tissues as well. It was concluded that sulfur played no role in the mortalities in Strang's Hatchery.

CONCLUSIONS

The lesson from this event is that the toxicological expertize of Department of Fisheries and Oceans should be called on before problems develop in aquaculture facilities. In this case, there is no doubt the recommendation would have been not to use a PVC liner.

The results obtained by other agencies and the cooperation of the suppliers of the liner were most helpful in the investigation. Water analyses ruled out Cu and Zn, and probably Cd as culprits. They were not sensitive enough to detect OBPA. The lack of bacteria, noted by the Disease & Nutrition investigators, indicated the presence of a germicide. This became a certainty once we identified the liner as a plasticized PVC. The plasticizer is the substrate on which fungi thrive and its presence renders the plastic susceptible to microbial attack. There are about five fungicides used in PVC (Yeager 1977): copper 8-quinolinate, OBPA, 2,3,5,6-tetrachloro-4-(methylsulfonyl)-pyridine, N-(trichloromethylthio)phthalimide, and N-(trichloromethylthio)tetrahydrophthalimide. OBPA is the one used most frequently and the confirmation of its presence by the industry eliminated the need to follow other leads.

PICI was an invaluable tool for the identification of phthalates. NICI did not provide useful information on phthalates, but readily detected hexachlorobenzene in the fish. This is a common trace contaminant of fish in our area.

We did not study in detail the kinetics of OBPA leaching from the liner. The results of such a study would very much depend on experimental conditions. It is obvious that with sufficient dilution OBPA will not cause mortalities. At the same time, its sublethal effects are unknown and it seems that the simplest solution by far is not to use it in aquaculture.

The variety of organic compounds identified or tentatively identified, as well as those not identified, brings up the question of their chronic effects during long-term exposure. Many are probably harmless but others are not, and their effects may become apparent in the long run. The problems of chemicals in aquacultural operations deserve considerable attention (see also Zitko 1981).

ACKNOWLEDGMENTS

Department of Fisheries and Oceans Scotia-Fundy Environmental Coordination arranged the analysis of water samples at the Laboratory Division, Air & Water Branch of Environmental Protection Service, Atlantic Region, Halifax, N. S., and at the Water

Quality Laboratory of Inland Waters, Moncton, N. B. Samples of fish and fish food were investigated by the Department of Fisheries and Oceans, Scotia-Fundy Disease & Nutrition Section. Mr. H. Akagi recorded the IR spectra. The following were very helpful and provided us with samples, advice, and information: Strang's Salmonid Hatchery, Fundy Park Rd., Penobsquis, N. B., E0E 1L0, telephone 506-433-1597; Louis White, Sr., Atlantic Smolts Ltd., Box 1, Site 5, Minto, N. B., E0E 1J0; Scarborough Canvas Ltd., 2071 McGowan, Agincourt, Ontario, M1S 3Y6, (Mr. R. MacKinnon, telephone 416-292-8006); Canadian General Tower Ltd., 52 Middleton Street, Cambridge, Ontario, N1R 5T6, (Gary Lloyd, telephone 416-823-7301); Mr. Solly Gagnon, Canadian General Tower Ltd., and Mr. A. L. Norris, Jr., Technical Manager, Analytical Services/QC, telephone 617-774-3100. Drs. R. L. Saunders and R. H. Peterson commented on the manuscript. The manuscript was edited by Ms. R. Garnett, formatted by Mrs. B. Garnett, and proofread by Ms. M. M. Irwin and Ms. R. Garnett.

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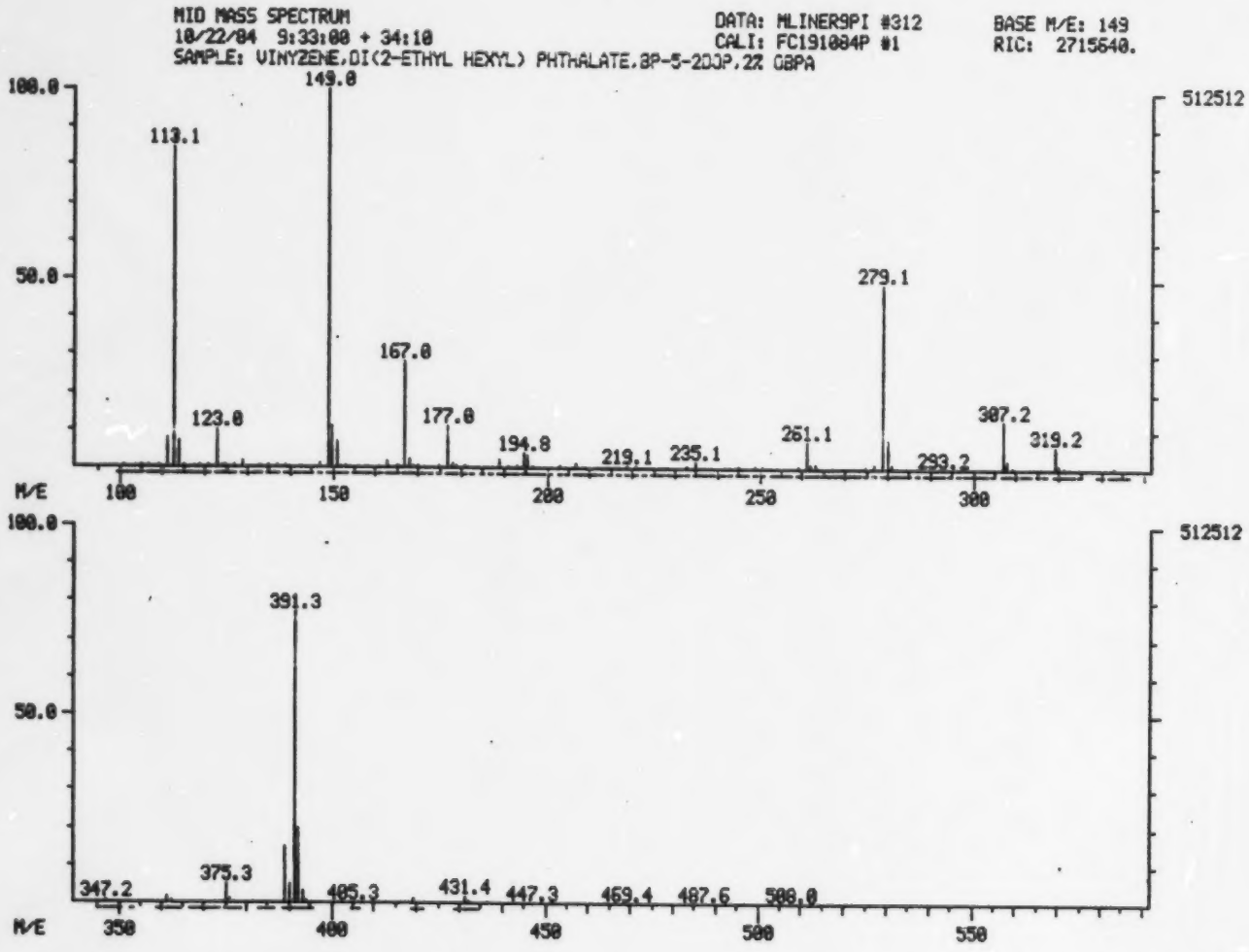

Fig. 1. PICI mass spectrum of di(2-ethylhexyl)phthalate.

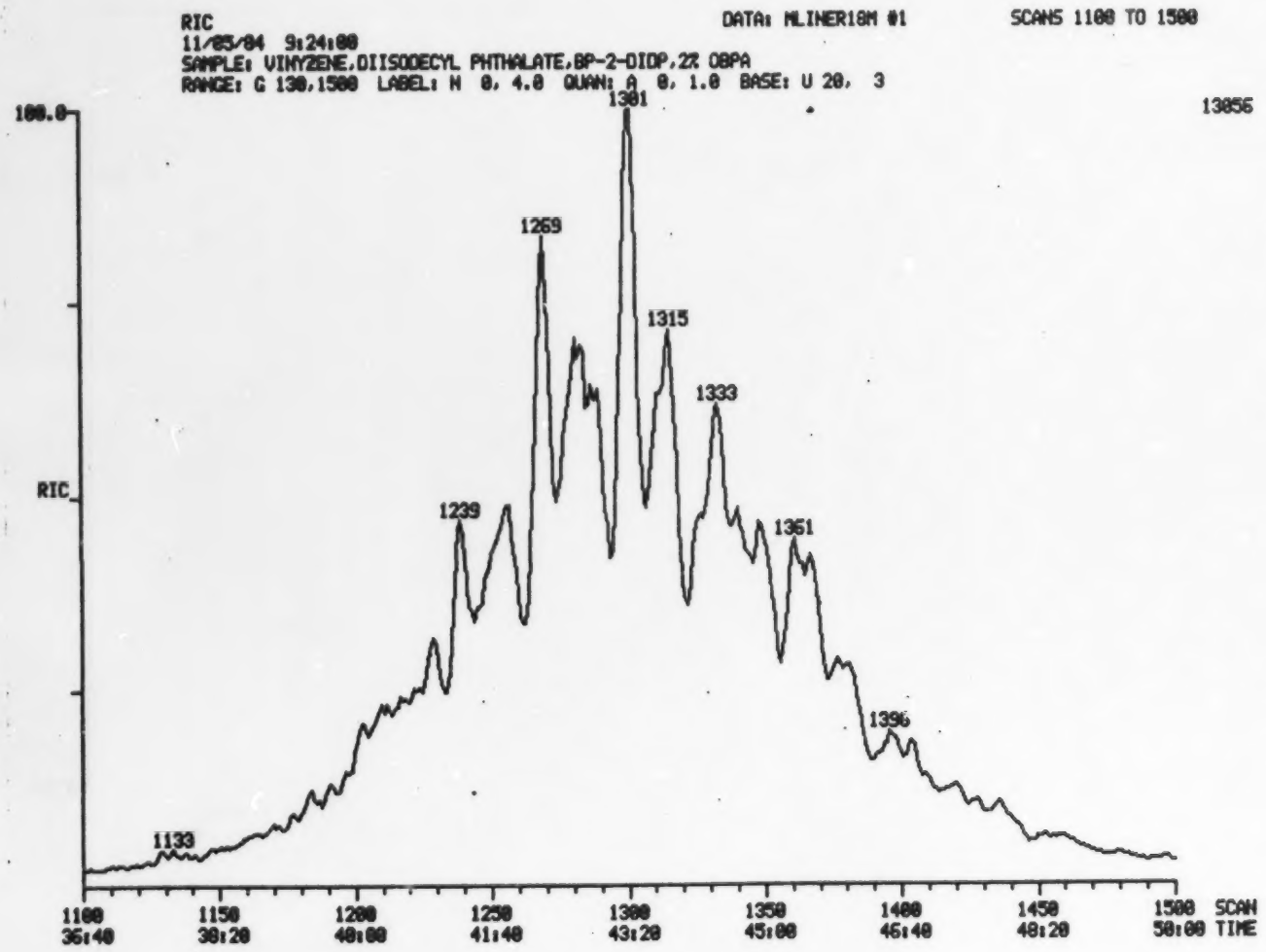

Fig. 2. Reconstructed gas chromatogram of VINYZENE(R) BP-5-2DIDP.

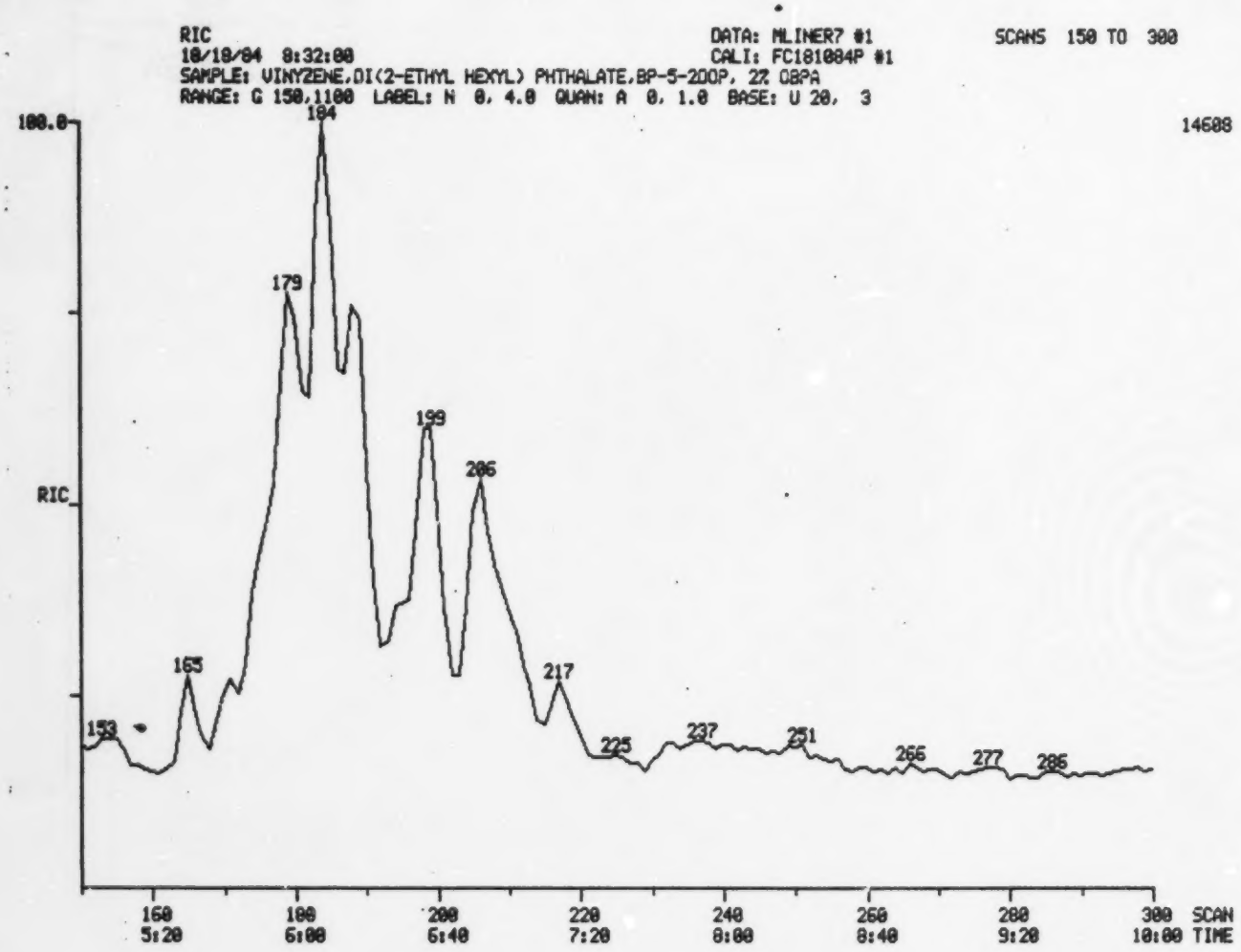

Fig. 3. Reconstructed gas chromatogram showing alcohols in VINYZENE(R) BP-5-2DOP.

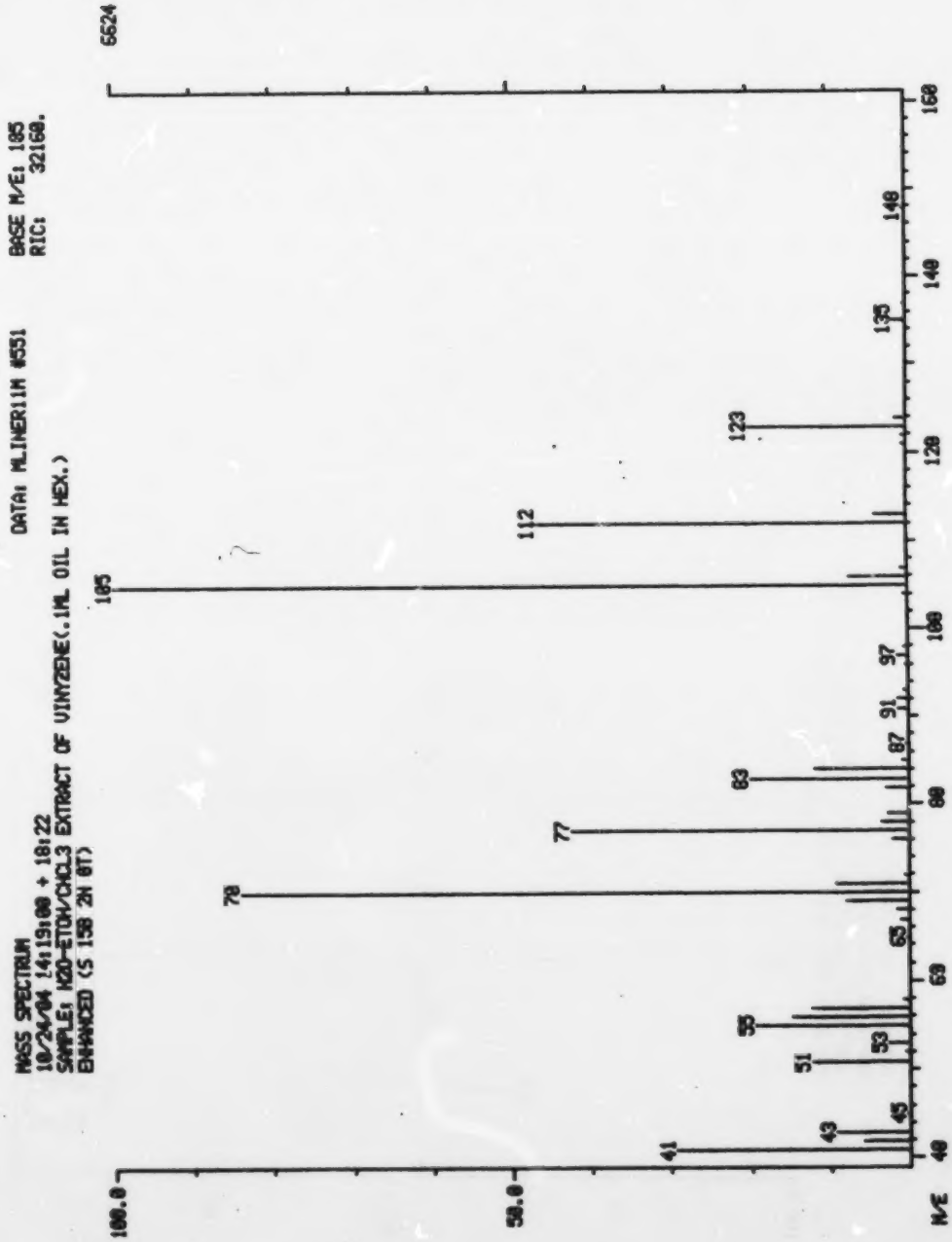

Fig. 4. Mass spectrum of pentyl benzoate.

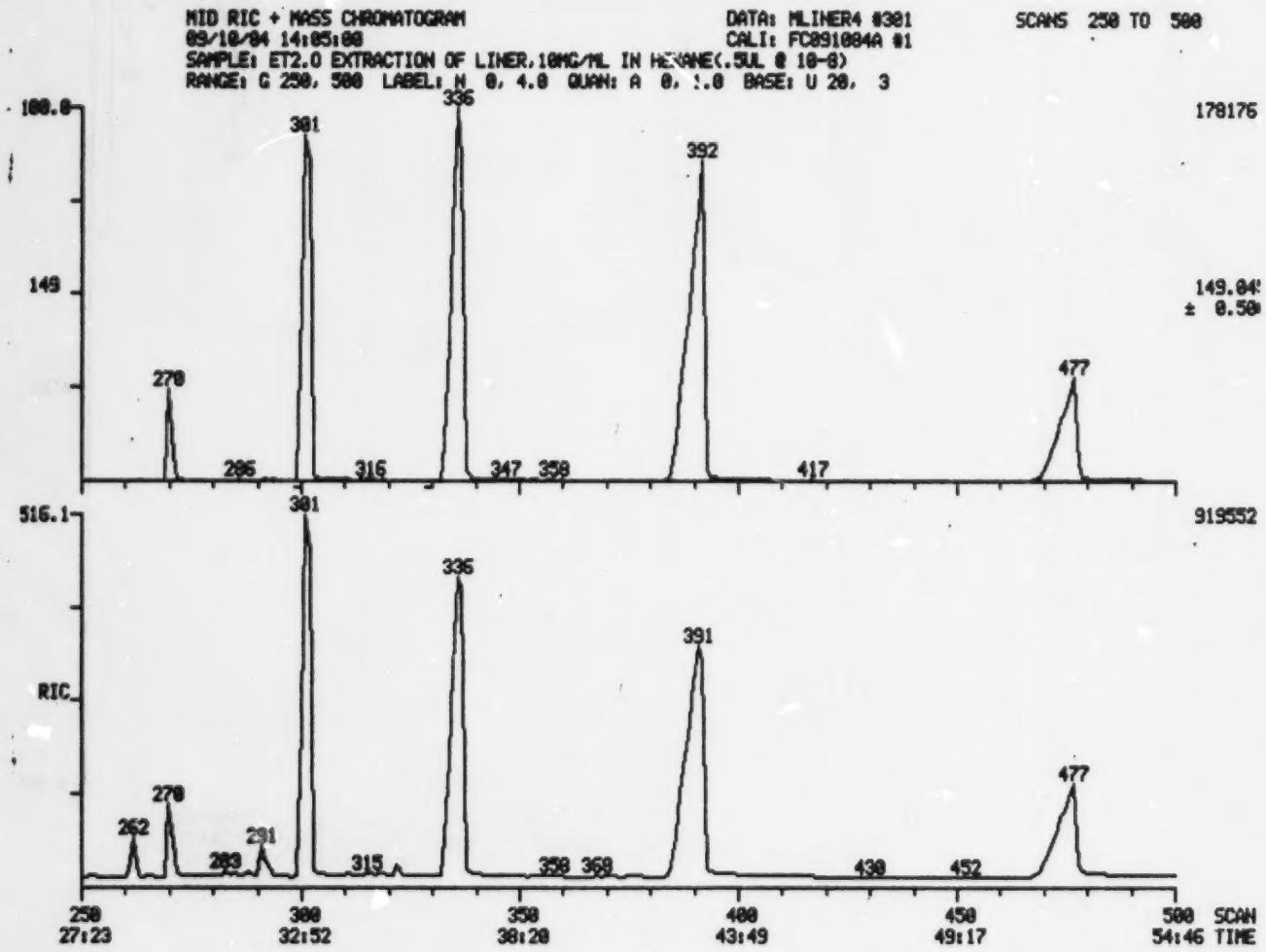

Fig. 5. Reconstructed gas chromatogram of ether extract of the "thick" liner. Ions at m/z=149 are typical for phthalates.

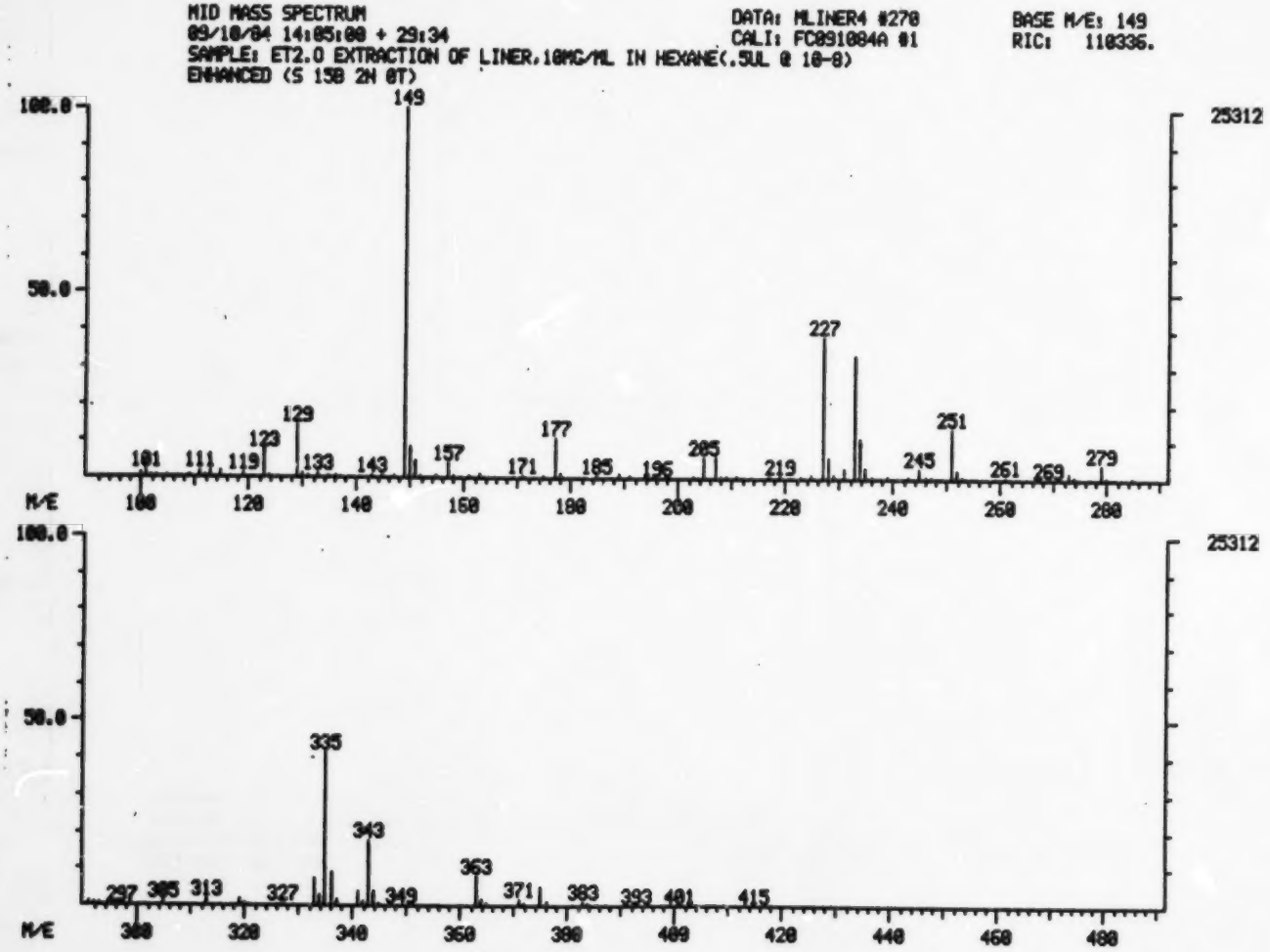

Fig. 6. PICI spectrum of a dihexyl phthalate.

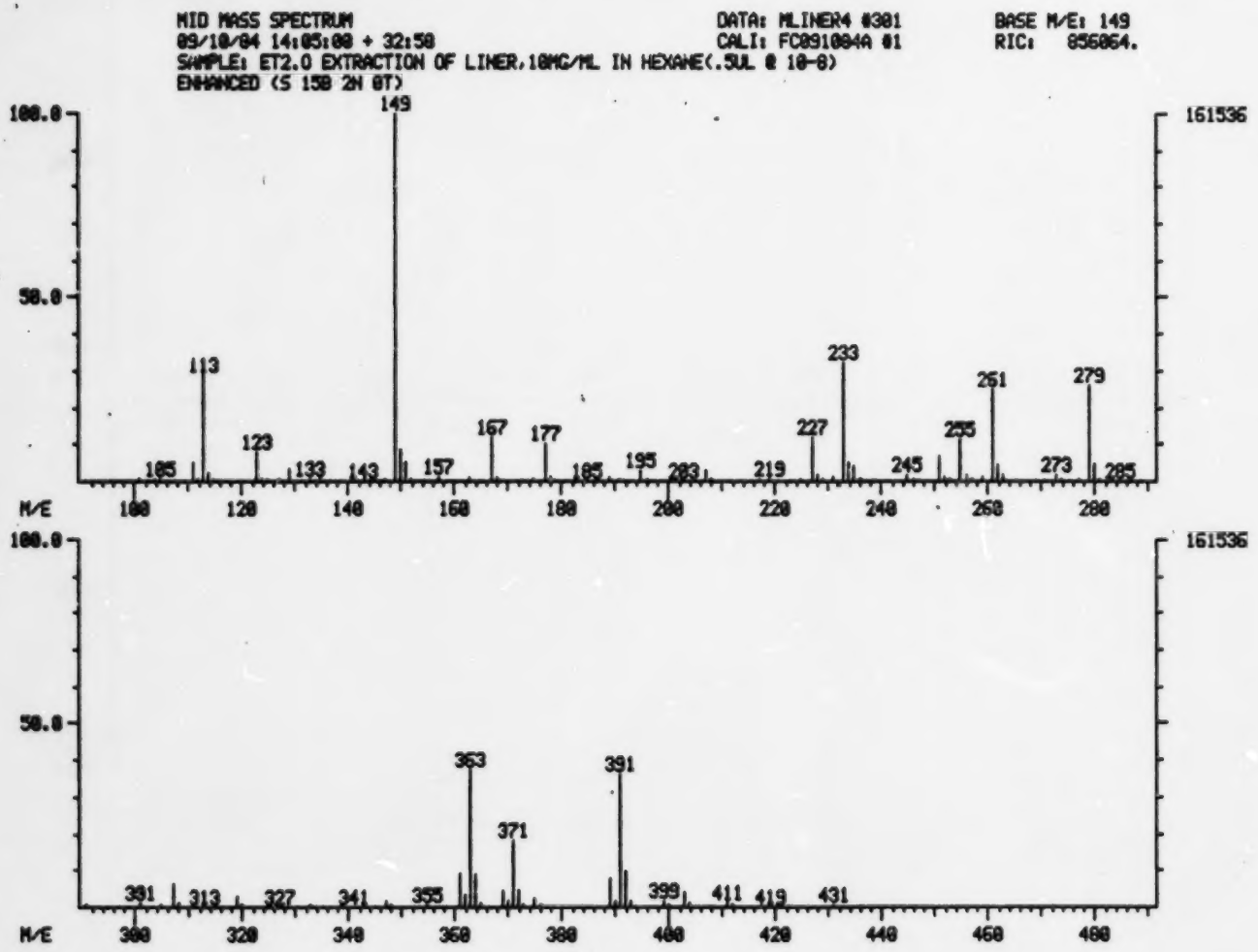

Fig. 7. PICI spectrum of a diheptyl and dioctyl phthalates.

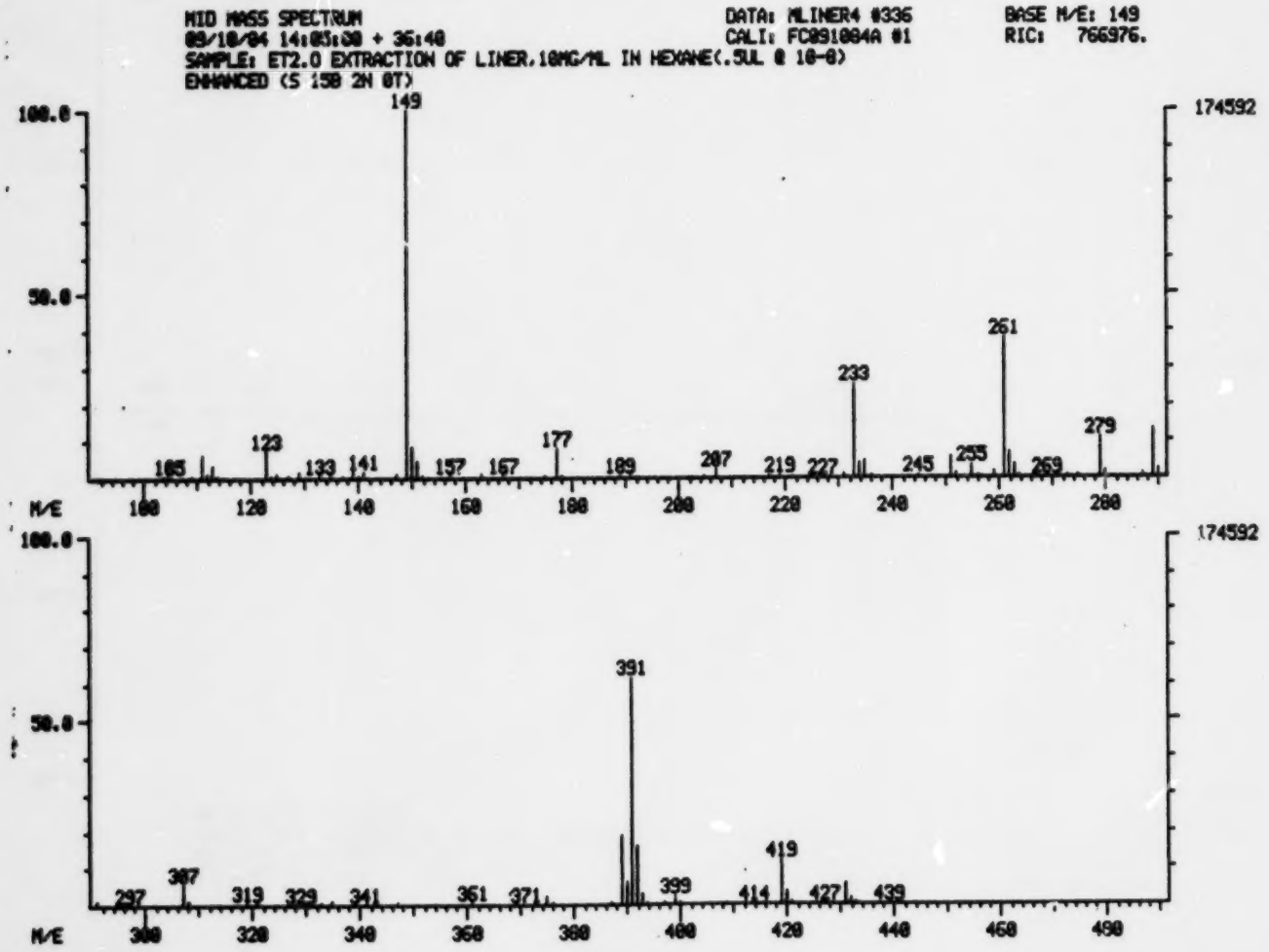

Fig. 8. PICI spectrum of a dioctyl and dinonyl phthalates.

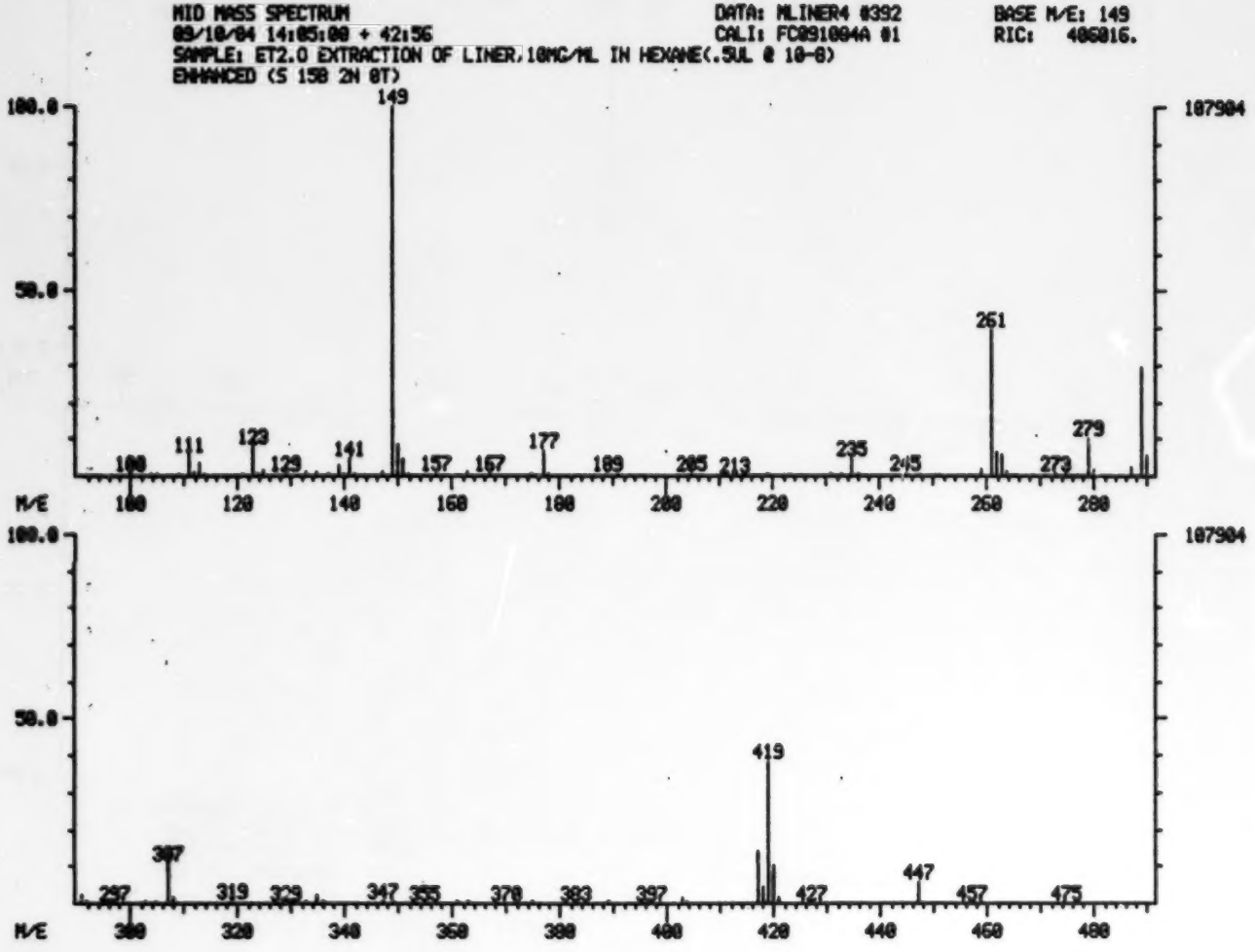

Fig. 9. PICI spectrum of a dinonyl phthalate.

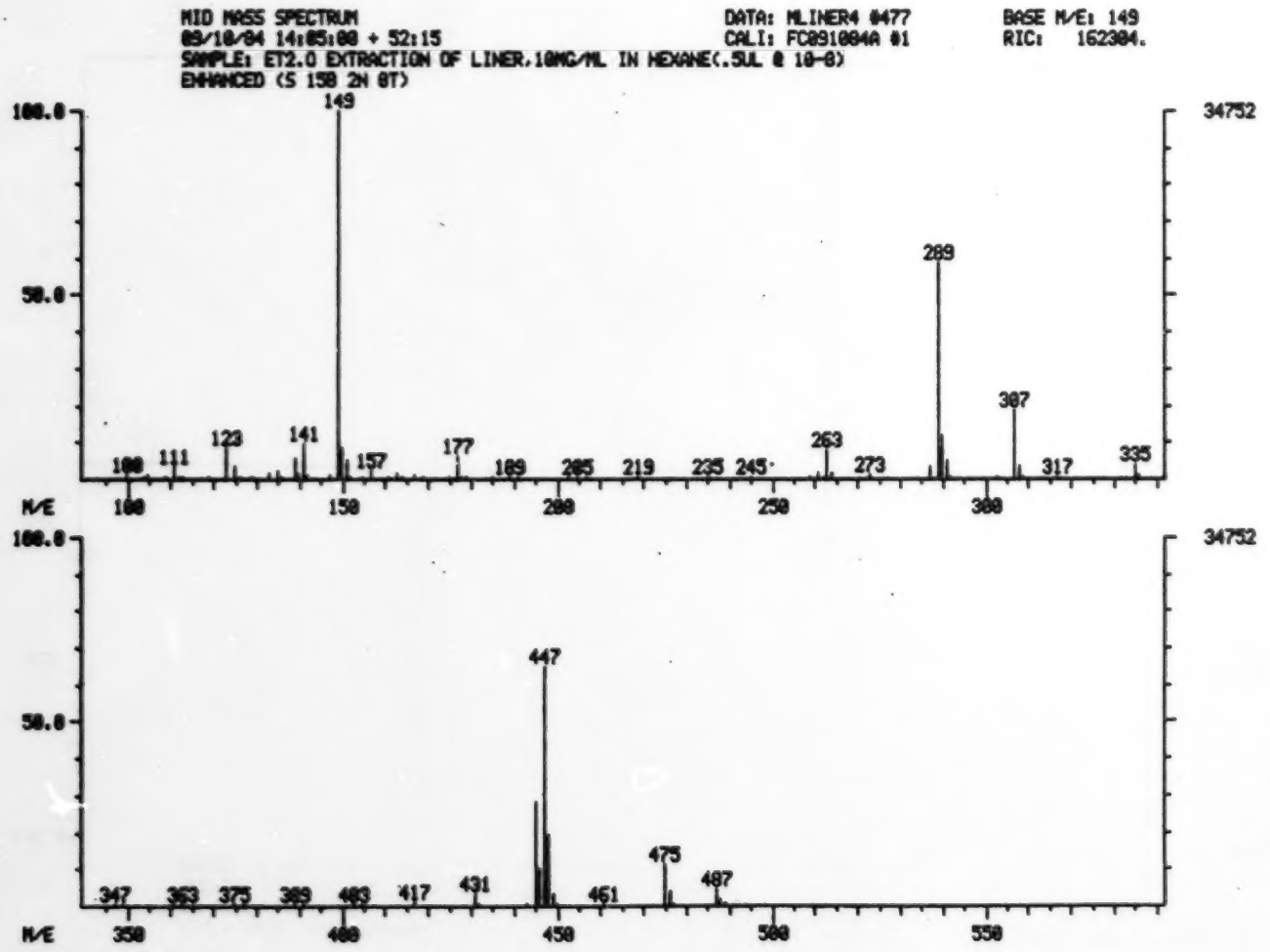

Fig. 10. FICI spectrum of a didecyl and diundecyl phthalates.

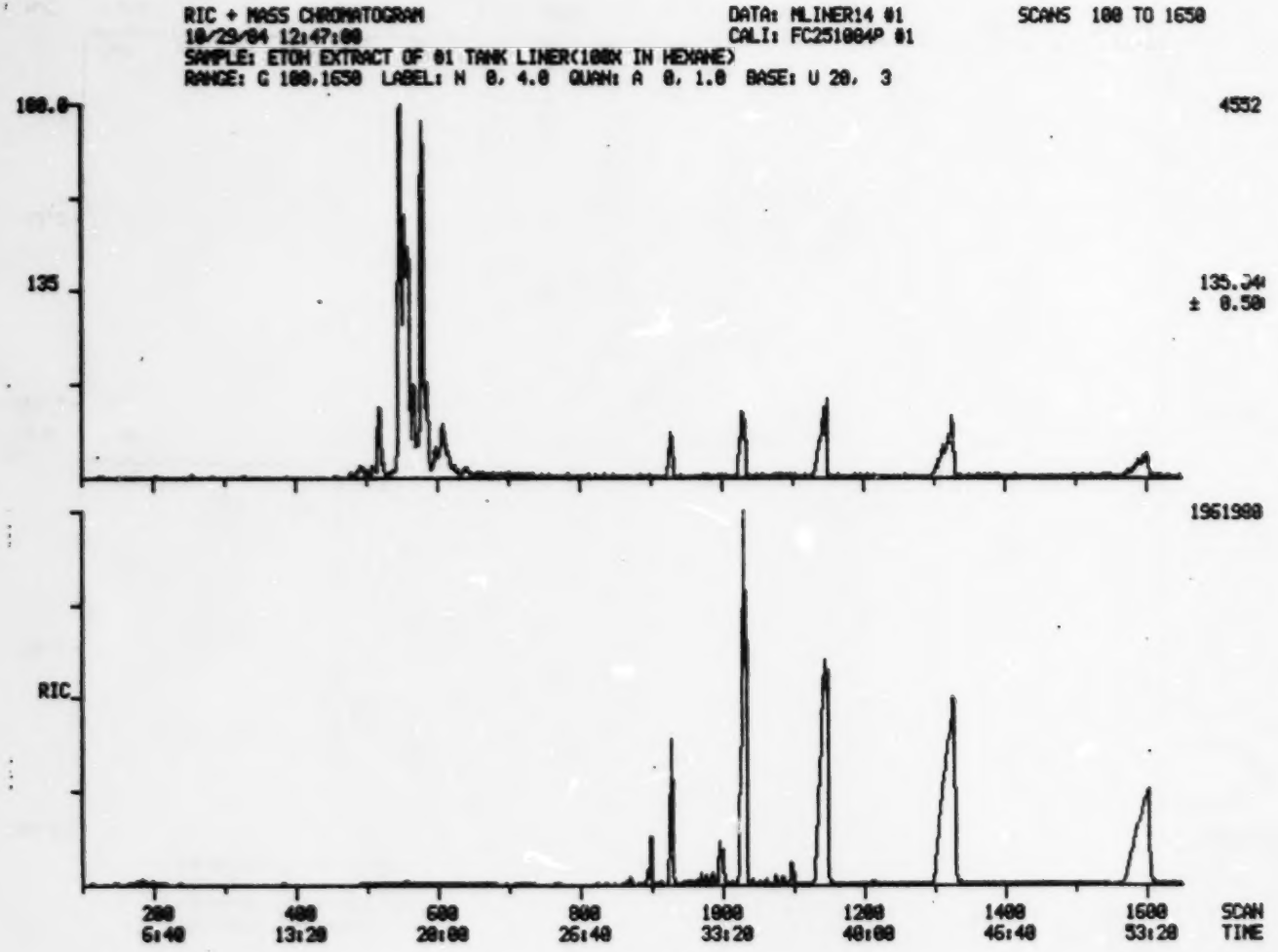

Fig. 11. Reconstructed gas chromatogram of ethanol extract of the liner. Ions at m/z=135 are characteristic of alkylphenols.

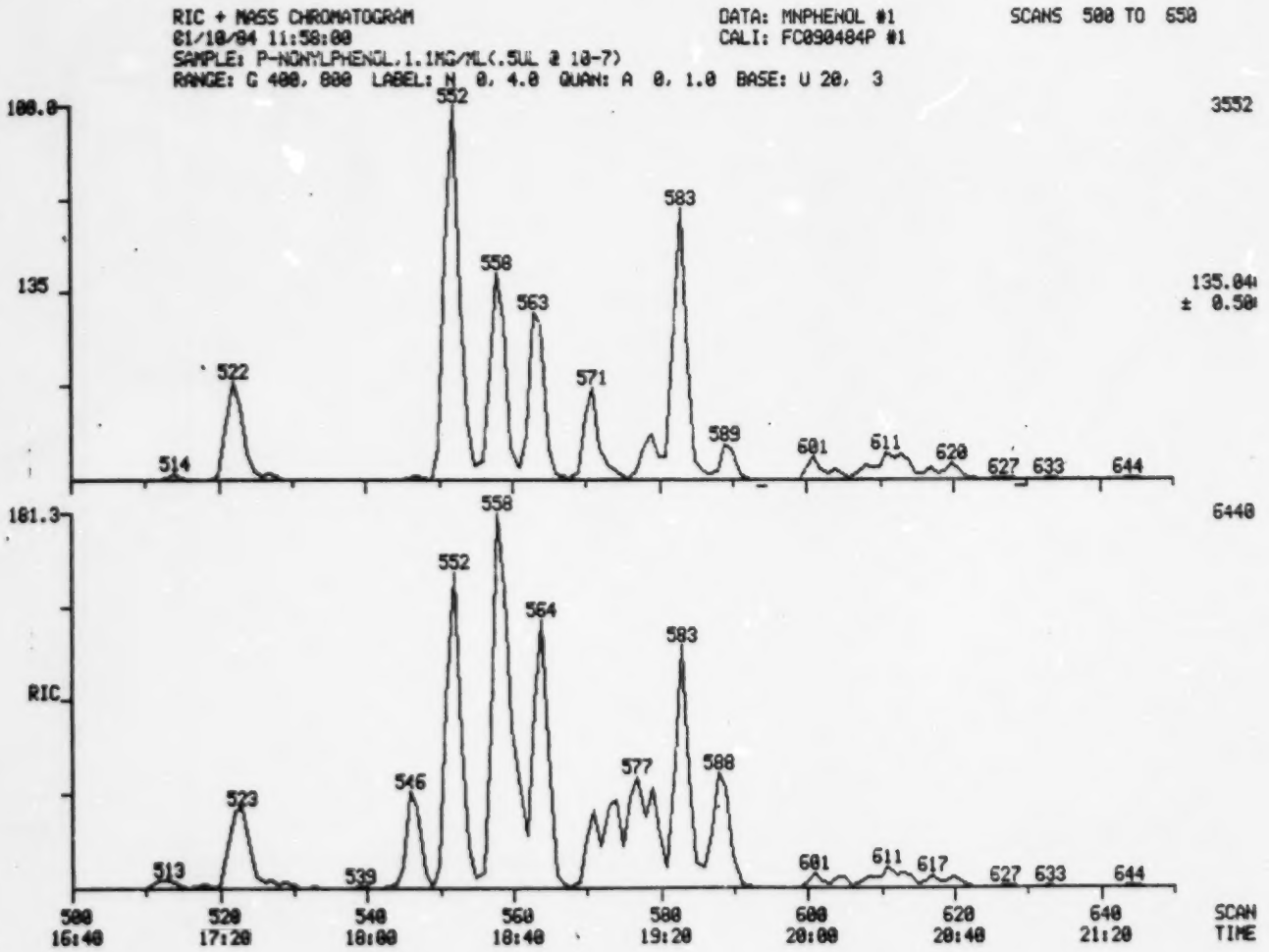

Fig. 12. Reconstructed gas chromatogram of nonylphenol.

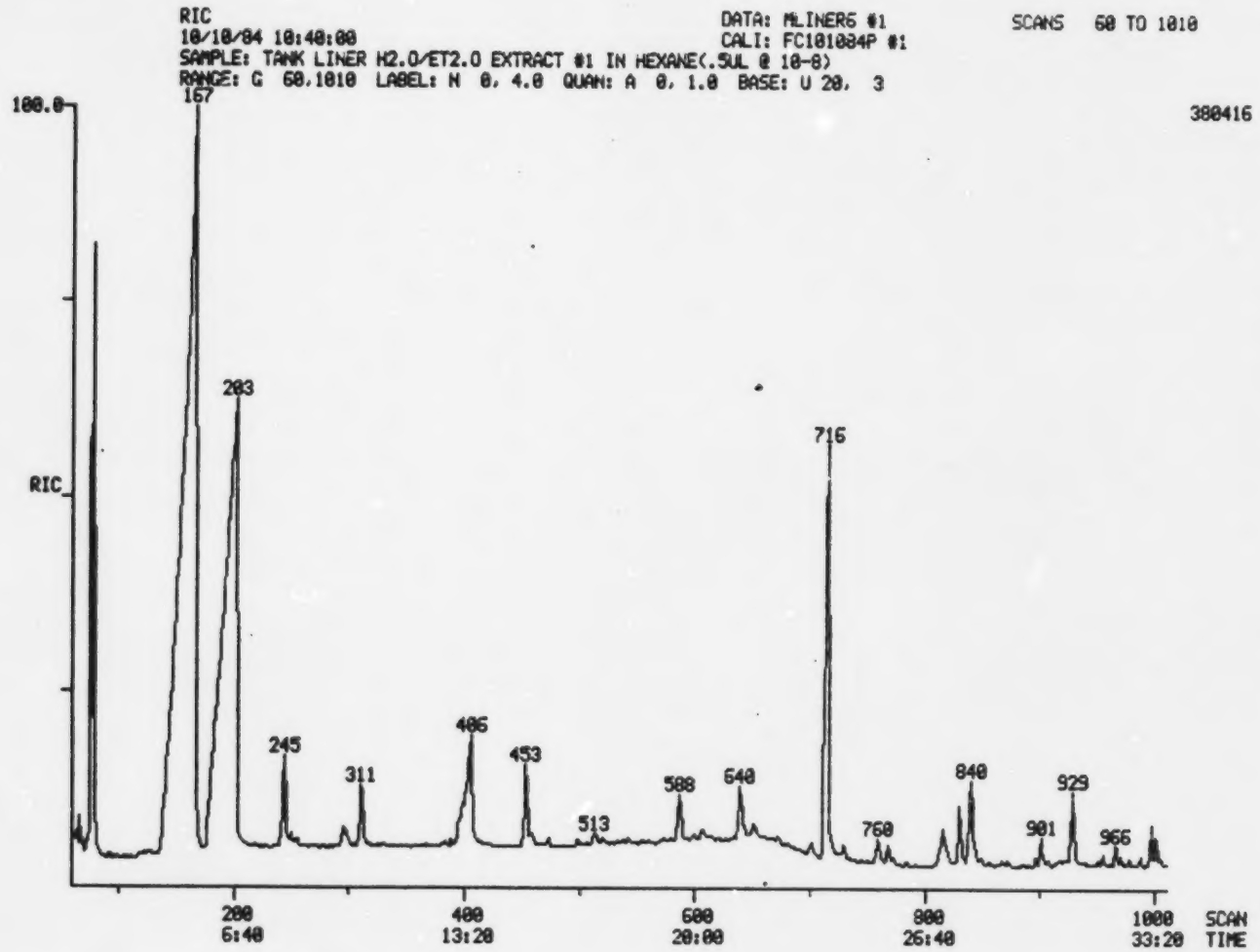

Fig. 13. Reconstructed gas chromatogram of compounds extracted from "thick" liner by boiling water. Scan 167 - 2-ethylhexanoic acid, 79 - phenol, 203 - benzoic acid, 716 - hexadecanoic acid.

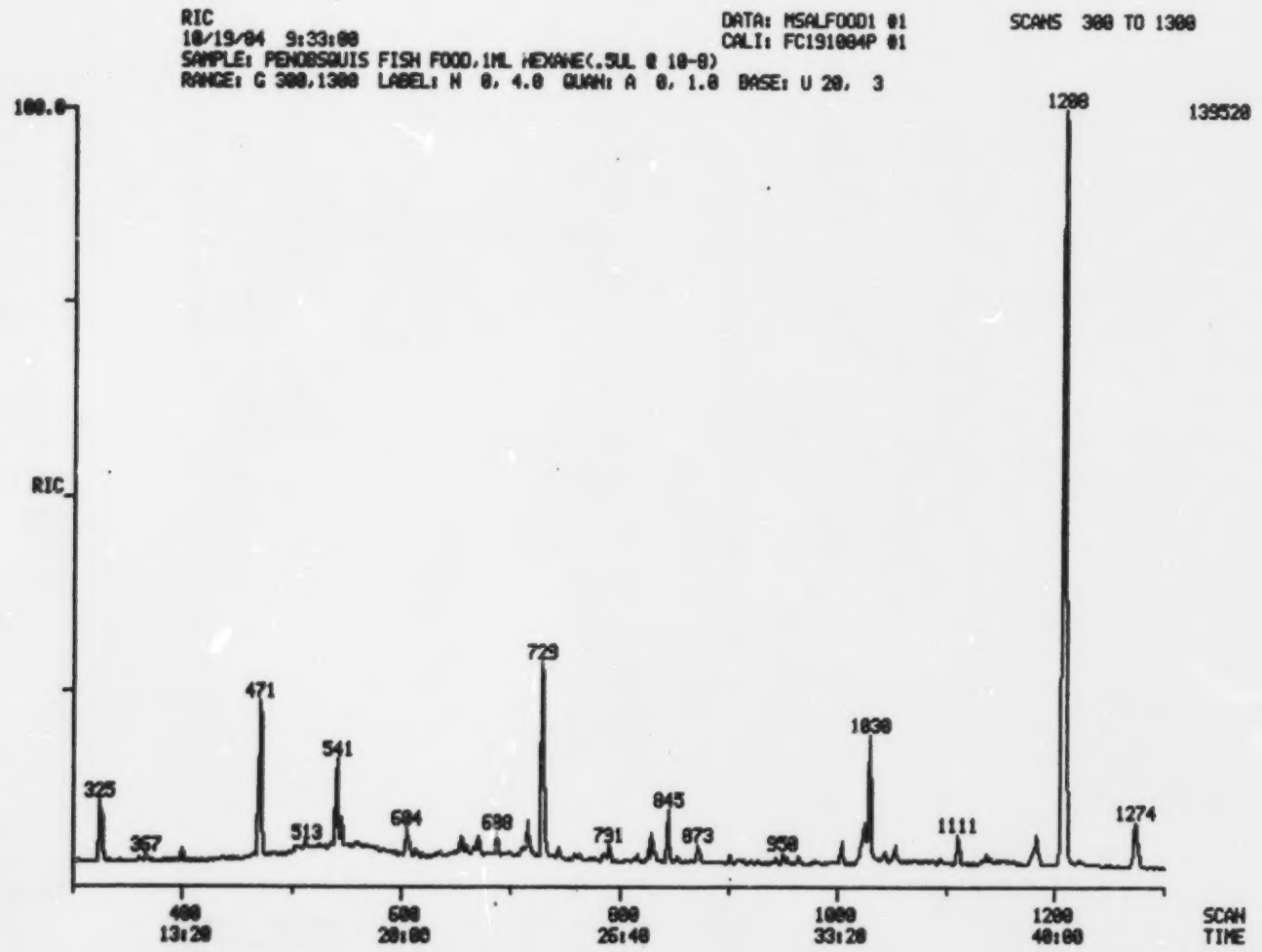

Fig. 14. Reconstructed gas chromatogram of fish food extract.
Scan 1208 - squalene, 729 - hexadecanoic acid ethyl ester, 471 - hexadecane, 1030 - DEHP.

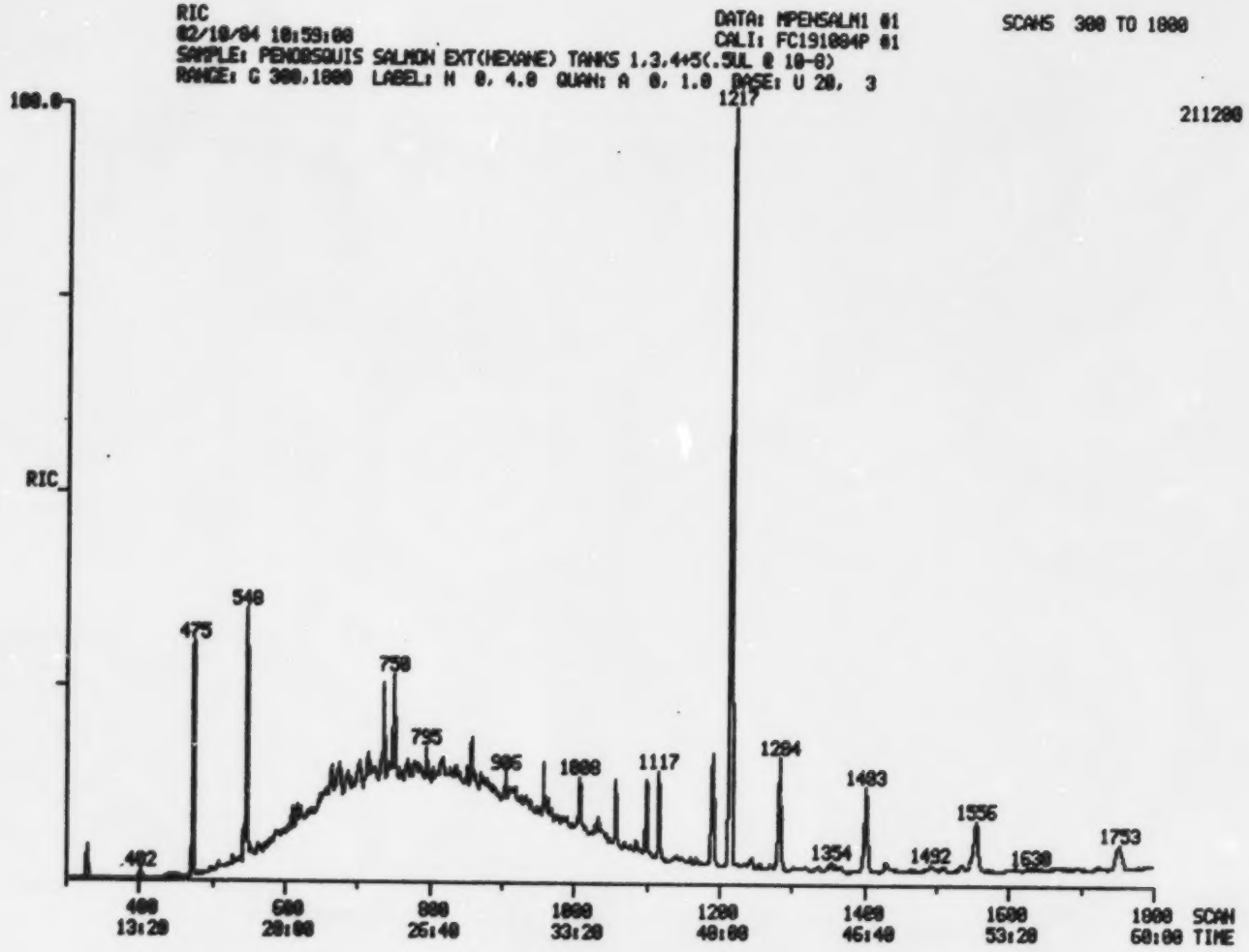

Fig. 15. Reconstructed EI gas chromatogram of salmon extract.
Scan 1217 - squalene, 475 - hexadecane, 548 - pristane 750 - elemental sulfur, 1100 - unidentified.

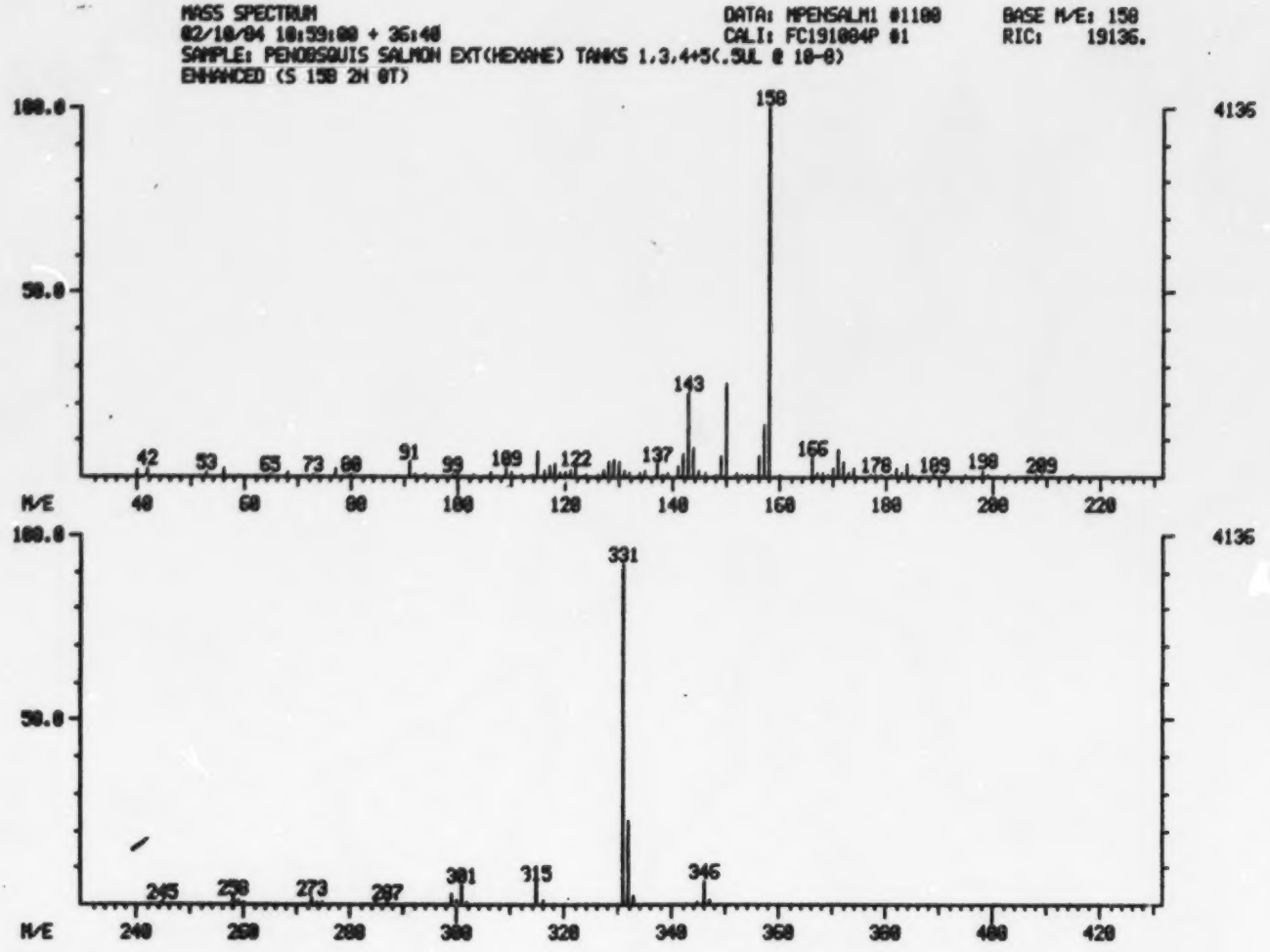

Fig. 16. EI mass spectrum of unidentified compound in scan 1100.

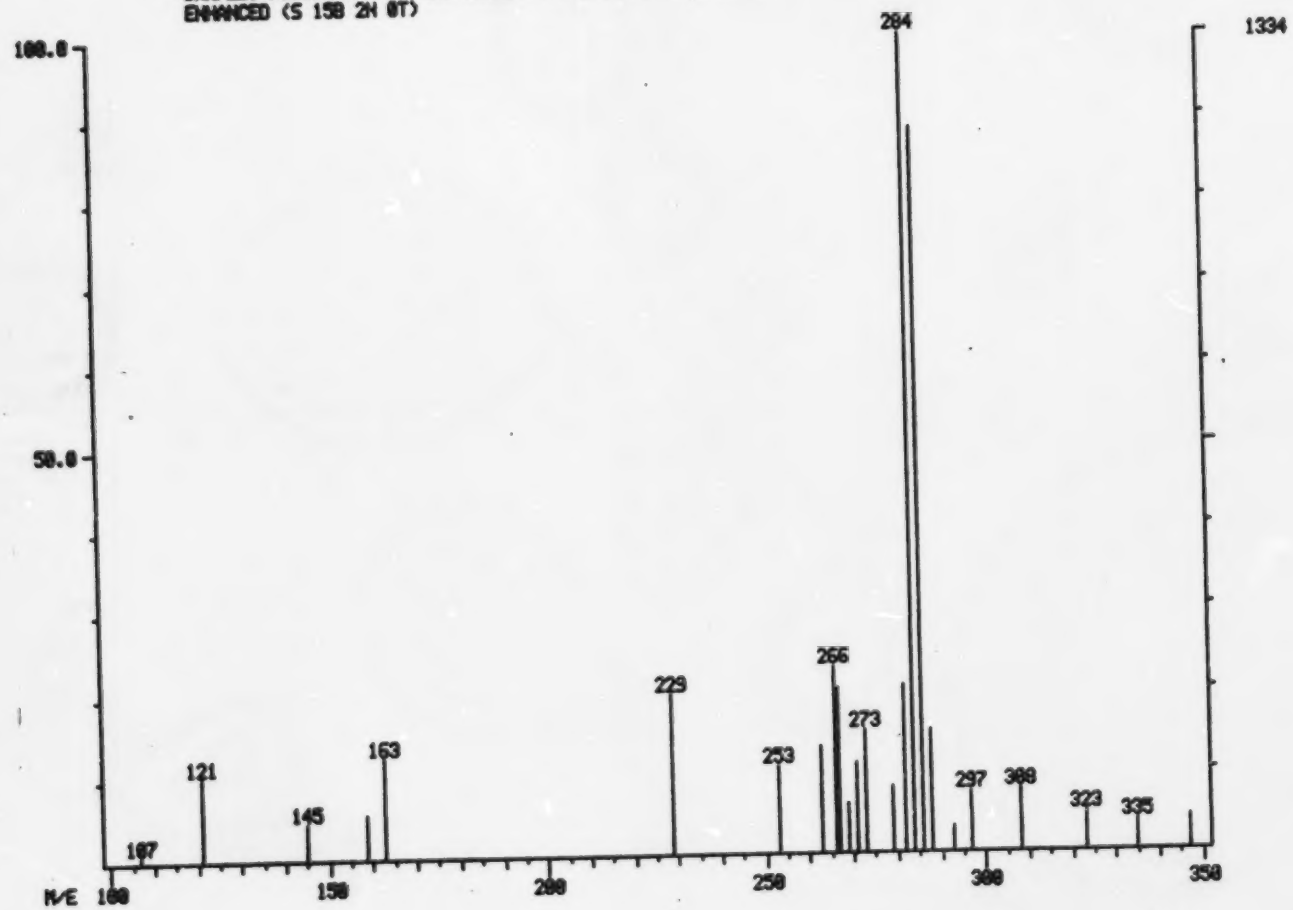

Fig. 17. NICI detection of hexachlorobenzene in salmon extract. Cl6 cluster at m/z 282.

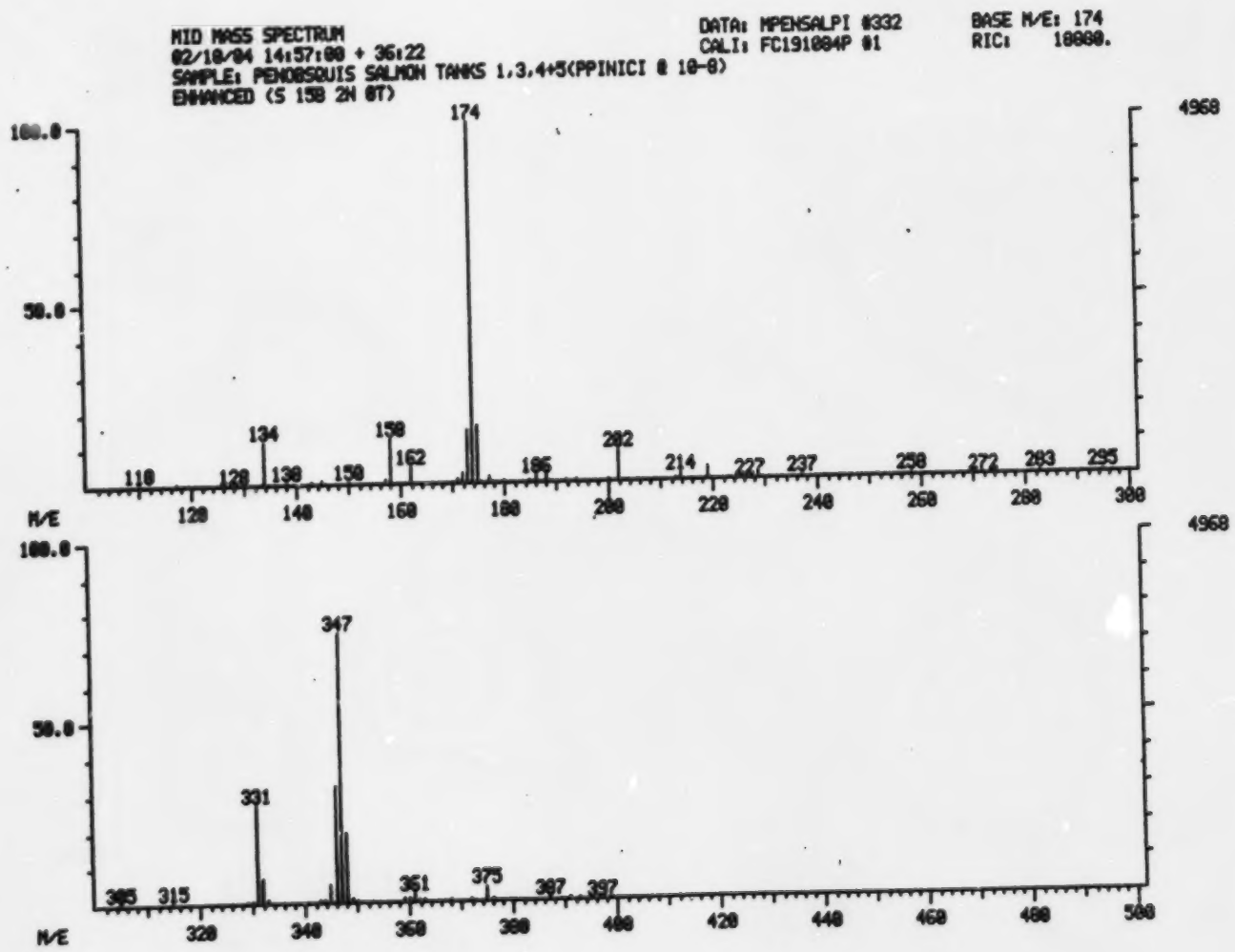

Fig. 18. PICI mass spectrum of unidentified compound in scan 1100.

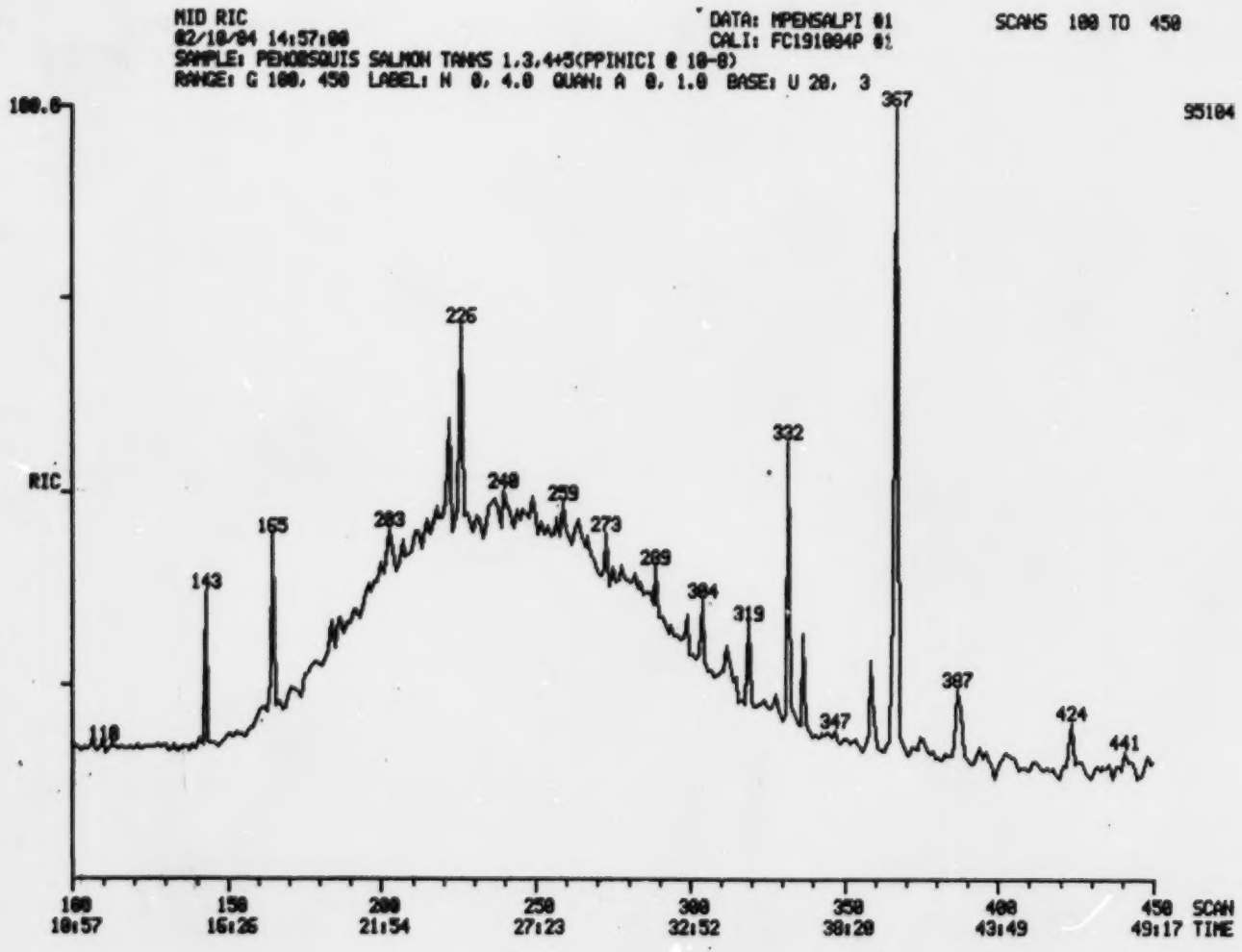

Fig. 19. Reconstructed PICI gas chromatogram of salmon extract. Compare with Fig. 15 for effect of ionization mode. Scan 367 - squalene, 332 - unidentified (1100 in EI), 143 - hexadecane, 165 - pristane, 226 - elemental sulfur.

APPENDIX

TOXICITY TEST HIGHLIGHTS

1) LINER #1 (Strang's)

11.1 g liner #1/3L H_2O		4 dead (3.07 g)	<45.25 h	4 control (1.89 g)
h	0	24	45.25	
Cd µg/L	0.3	1.5	0.4	
Cu			0.01 µg/g	
Pb			Detectable	
Zn			Detectable	

2) LINER #1 (Strang's)

11.07 g liner #1/3L H_2O	4 dead (2.93 g)	<47 h	4 control (1.77 g)
h 0	24	47	LT50 = 35 h
Cd µg/L	1.3	1.4	
As		29	

3) ETHER EXTRACT OF LINER #1 (Strang's)

2 mL stock (25.6 mg/mL)/3L H_2O [17.07 mg/L]	none died in 96 h

4) ETHANOL EXTRACT OF LINERS #2 & #3

2 mL 49.26 mg/mL stock evaporated on flask bottom				none died in 96 h
h		24		
Cd µg/L		3.6		
As µg/L		7.7		
2 mL 229.6 mg/mL stock evaporated on flask bottom				3 died (2.9 g) <47 h LT50=25
h	4.25	28	47.25	
As µg/L	44.7	45.9	36.0	
1 mL 229.6 mg/mL stock evaporated on flask bottom				3 died (3.5 g) <69 h LT50=60
h		45	69	
As µg/L		35.1	34.9	

Fish remained alive at max of 11.3 µg/L As

5) VINYZENE(R) BP-5-2DOP

0.28 mL/3L H_2O [90 mg/L]		4 dead (3.1 g)	<3.75 h	LT50=3 h
h	4			
As µg/L	212			

VINYZENE(R) BP-5-2DIDP

0.28 mL/3L H_2O [90 mg/L]		3 dead (6.9 g)	<2.25 h			LT50=2 h	
h	0	2	24	48	72	120	168
As µg/L	202	257	187	166	247		150

VINYZENE(R) BP-5-2DOP DEGRADATION - NO FISH

0.28 mL/3L H_2O [90 mg/L]							
h	0	2.5	24	48	72	120	168
As µg/L	143	166	244	280	234		

VINYZENE(R) BP-5-2DIDP DEGRADATION - NO FISH

0.28 mL/3L H_2O [90 mg/L]							
h	0	2.5	24	48	72	120	168
As µg/L			210	163	268	311	481

6) VINYZENE(R) BP-5-2DIDP

0.100 mL/3L H_2O [33.3 mg/L]	killed 3 fish (7.0 g) in <5.25 h
0.050 mL/3L H_2O [16.5 mg/L]	killed 3 fish (5.6 g) in <6 h
0.025 mL/3L H_2O [8.25 mg/L]	killed 3 fish (7.4 g) in <5.25 h
0.013 mL/3L H_2O [4.2 mg/L]	killed 3 fish (6.8 g) in <12 h

APPENDIX (cont'd.)

7) VINYZENE(R) BP-5-2DOP WITH OBPA REMOVED

0.28 mL pooled extract/3L [90 mg/L] no deaths (5.83 g) in 96 h

h	5.75	29	96
Cd µg/L	0.1	0.1	Detectable
As µg/L			9

8) Cd STEARATE

0.07 g/g Ottawa sand (10 g sand/flask) [0.233 g/L] 1 fish (5.9 g) dead <95 h
Cd no sampling done

0.07 g/g Ottawa sand (5 g sand/flask) [0.1165 g/L] 1 fish (6.3 g) dead <96 h

h	0	3	6	12	24	48	72	96
Cd µg/L	299	559	380	1750	1860	531	1640	451
	349				1570			910

9) VINYZENE(R) BP-5-2DIDP

0.41 mg/L No fish died
As µg/L about 2; not readily detectable

approx 5 mg/L LT50=9 h (2/3 dead at 12 h and 3/3 dead at 24 h)

h	0	3	6	12	24
As µg/L	30.6	24.4	32.9	19.0	22.3

approx 2 mg/L no deaths by 96 h

h	0	3	6	12	24	48
As µg/L	14.8	10.3	11.1	9.4	8.5	5.4

10) LINER #2 (Strang's)

11.07 g liner/3L H_2O all 3 dead (5.07 g) <50 h LT50=38 h

11) LINER #3 (Strang's)

11.10 g liner/3L H_2O all 3 dead (4.57 g) <95 h LT50=63 h

12) LINER #4 (Strang's)

11.07 g liner/3L H_2O 1/3 dead (4.57 g) <96 h

13) ETHER EXTRACT LINER #2 (Strang's)

6 mL stock (72 mg/mL)/3L 0/3 dead (5.3 g) at 96 h

h	0	3	6	12	24	48
As µg/L	17.8	20.6	20.9	18.5	16.5	15.8

1.5 mL stock/3L 0/3 dead (4.6 g) at 96 h

h	0	3	6	12	24	48
As µg/L	6.14	4.62	4.69	5.61	3.15	4.47

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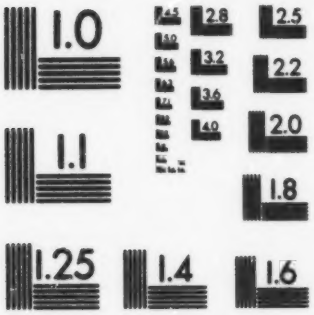

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A Five-year Summary (1978-1982) of the Nestling Diet of Cassin's Auklets in British Columbia

Kees Vermeer
Canadian Wildlife Service

Institute of Ocean Sciences
Department of Fisheries and Oceans
Sidney, B.C. V8L 4B2

1985

Canadian Technical Report of Hydrography and Ocean Sciences No. 56

-4236/

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Regional and headquarters establishments of Ocean Science and Surveys ceased publication of their various report series as of December 1981. A complete listing of these publications and the last number issued under each title are published in the *Canadian Journal of Fisheries and Aquatic Sciences*, Volume 38: Index to Publications 1981. The current series began with Report Number 1 in January 1982.

Rapport technique canadien sur l'hydrographie et les sciences océaniques

Ces rapports contiennent des renseignements scientifiques et techniques qui constituent une contribution aux connaissances actuelles mais que l'on ne trouve pas normalement dans les revues scientifiques. Le sujet est généralement rattaché aux programmes et intérêts du service des Sciences et Levés océaniques (SLO) du ministère des Pêches et des Océans.

Les rapports techniques peuvent être considérés comme des publications à part entière. Le titre exact figure au-dessus du résumé du chaque rapport. Les résumés des rapports seront publiés dans la revue Résumés des sciences aquatiques et halieutiques et les titres figureront dans l'index annuel des publications scientifiques et techniques du Ministère.

Les rapports techniques sont produits à l'échelon régional mais sont numérotés et placés dans l'index à l'échelon national. Les demandes de rapports seront satisfaites par l'établissement auteur dont le nom figure sur la couverture et la page de titre. Les rapports épuisés seront fournis contre rétribution par des agents commerciaux.

Les établissements des Sciences et Levés océaniques dans les régions et à l'administration centrale ont cessé de publier leurs diverses séries de rapports depuis décembre 1981. Vous trouverez dans l'index des publications du volume 38 du *Journal canadien des sciences halieutiques et aquatiques*, la liste de ces publications ainsi que le dernier numéro paru dans chaque catégorie. La nouvelle série a commencé avec la publication du Rapport n° 1 en janvier 1982.

Canadian Technical Report of Hydrography and Ocean Sciences No. 56

1985

A FIVE-YEAR SUMMARY (1978-1982) OF THE NESTLING DIET OF CASSIN'S AUKLETS IN BRITISH COLUMBIA

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ABSTRACT

Vermeer, Kees. 1985. A five-year summary (1978-1982) of the nestling diet of Cassin's Auklets in British Columbia. Can. Tech. Rep. Hydrogr. Ocean Sci. No. 56 : iii + 15p.

Information on the nestling diet of Cassin's Auklets (Ptychoramphus aleuticus), collected on Triangle Island from 1978 through 1982, on Frederick Island in 1980 and 1981, and on Ramsay and Rankine islands in 1982, has been summarized. Nine prey categories were identified, of which calanoid copepods, euphausiids and fishes made up most of the meal biomass. The most important identified food species were Neocalanus cristatus, Thysanoessa spinifera, T. longipes and Euphausia pacifica. Fishes identified were Ammodytes hexapterus, Hemilepidotus sp., Sebastes sp., and Hexagrammos sp. Neither hyperiid amphipods, such as Parathemisto pacifica and Vibilia propingua, nor carideans, such as Pandalopsis dispar, Pandalus platyceros and Pasiphaea pacifica contstituted a major portion of Cassin's Auklet meals, although they frequently occurred in some years.

Key words: Cassin's Auklet, nestling diet, British Columbia

RÉSUMÉ

Vermeer, Kees. 1985. A five-year summary (1978-1982) of the nestling diet of Cassin's Auklets in British Columbia. Can. Tech. Rep. Hydrogr. Ocean Sci. No. 56 : iii + 15p.

On résume les données recueillies sur la régime allimentaire des oisillons de l'alque de Cassin (Ptychoramphus aleuticus) dans les îles Triangle (1978-1982), Frederick (1980-1981), Ramsay et Rankine (1982). Neuf categories de proies sont identifiées; les copépodes calanoïdes, les euphausiacés et les poissons constituaent presque toute la biomasse consommée. Parmi les proies, les espèces les plus importantes étaient Neocalanus cristatus, Thysanoessa spinifera, T. longipes et Euphausia pacifica. Pour ce qui est des poissons, Ammodytes hexapterus, Hemilepidotus sp., Sebastes sp. et Hexagrammos sp. étaient présents. Aucun amphipode hyperidé comme Parathemisto pacifica et Vibilia propingua ni caride comme Pandalopsis dispar, Pandalus platyceros et Pasiphaea pacifica ne constituaient une grande partie de la nourriture de l'alque de Cassin, mais ils étaient fréquemment presents certaines années.

Mots-clés: L'alque de Cassin, le regime alimentaire des oisillons, Colombie-Britannique.

INTRODUCTION

Cassin's Auklets (Ptychoramphus aleuticus, Fig. 1) are the most numerous nesting seabirds on Canada's west coast (Vermeer et al. 1983). Their total nesting population, which is found entirely in the northeastern Pacific Ocean, consists of as many as 900,000 breeding pairs, of which 62% utilize nesting islands on the British Columbia coast (Vermeer et al. 1979). As Cassin's Auklets constitute an important component of the seabird population and as there was little previous information on their nestling diet in British Columbia, I studied that subject from 1978 through 1982.

Cassin's Auklets bring zooplankton and fishes as food to their nestlings in a throat pouch. It is during the nestling period which generally occurs from the end of May to the end of July that prey can be adequately sampled, and changes in species and size with time determined. Aspects of the nestling diet of Cassin's Auklets on Triangle Island (50° 52'N; 125° 05'W) from 1978 through 1981 and on Frederick Island (53° 56'N, 133° 10'W) in 1980 and 1981 were previously reported by Vermeer (1981, 1985). Additional information on the nestling diet was obtained on Triangle, Ramsay (52°33'N; 131°22'W) and Rankine (52°15'N; 131°06'W) islands in 1982. The objectives here are to summarize the information on the nestling diet of Cassin's Auklets in British Columbia from 1978 through 1982, and to analyze the 1982 meal samples for hourly and seasonal variation in food composition. It is to be noted that the seasonal variation of the nestling diet from 1978 through 1981 has been discussed by Vermeer (1981, 1985).

METHODS

Food samples of Cassin's Auklets were collected, processed and identified as described by Vermeer (1981, 1985). Cassin's Auklet meals were collected on Triangle Island from about the end of May to the end of July in 1978 through 1981 and on Frederick Island during the same period in 1980 and 1981 (Table 1). In 1982, samples were collected on Triangle Island at 4 day intervals (Table 2) to determine if food varied in relation to the time the birds were captured. A limited number of samples were collected from auklets in 1982 on Ramsay and Rankine islands (Table 2), located in more shallow and sheltered waters than Triangle and Frederick islands for comparative purposes (Fig. 2). Differences between prey proportions were analyzed using 2x2 Contingency Tables.

RESULTS

A. Meals and meal sizes

The 998 Cassin's Auklet meals collected on the four islands from 1978 through 1982 weighed 19 kg (Tables 1 and 2). The average bird meal weighed 19 g. Individual values of weight varied from 17.6 to 21.2 g on Triangle Island from 1978 through 1982, and from 16.8 to 18.9 g on Frederick Island in 1980 and 1981 (Tables 3 and 4).

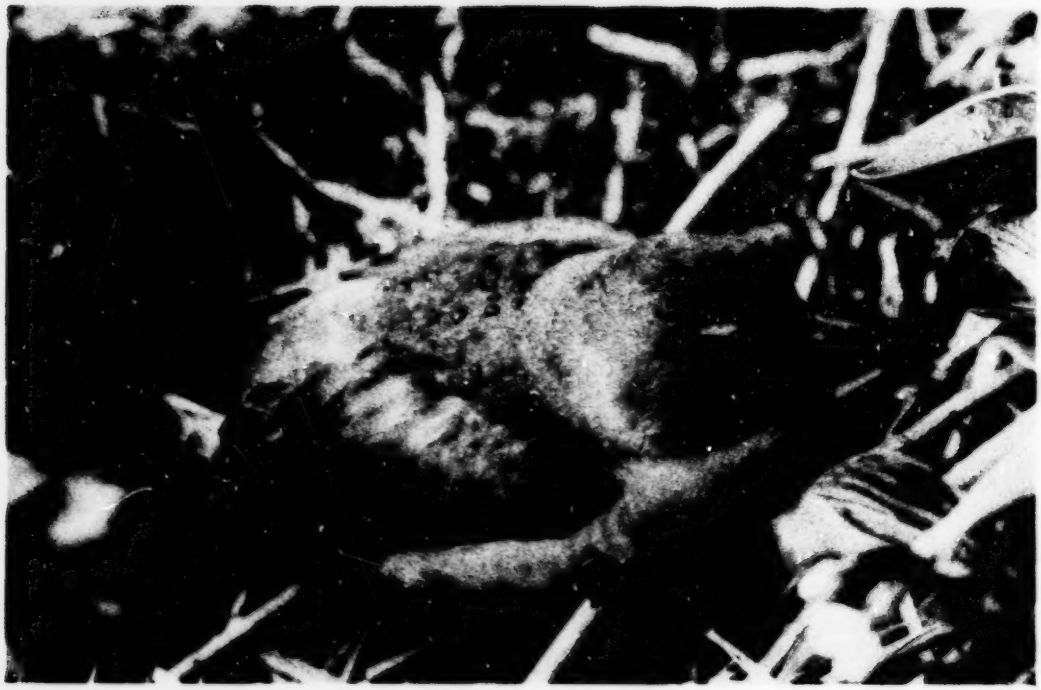

Figure 1. Adult Cassin's Auklet in nesting colony.

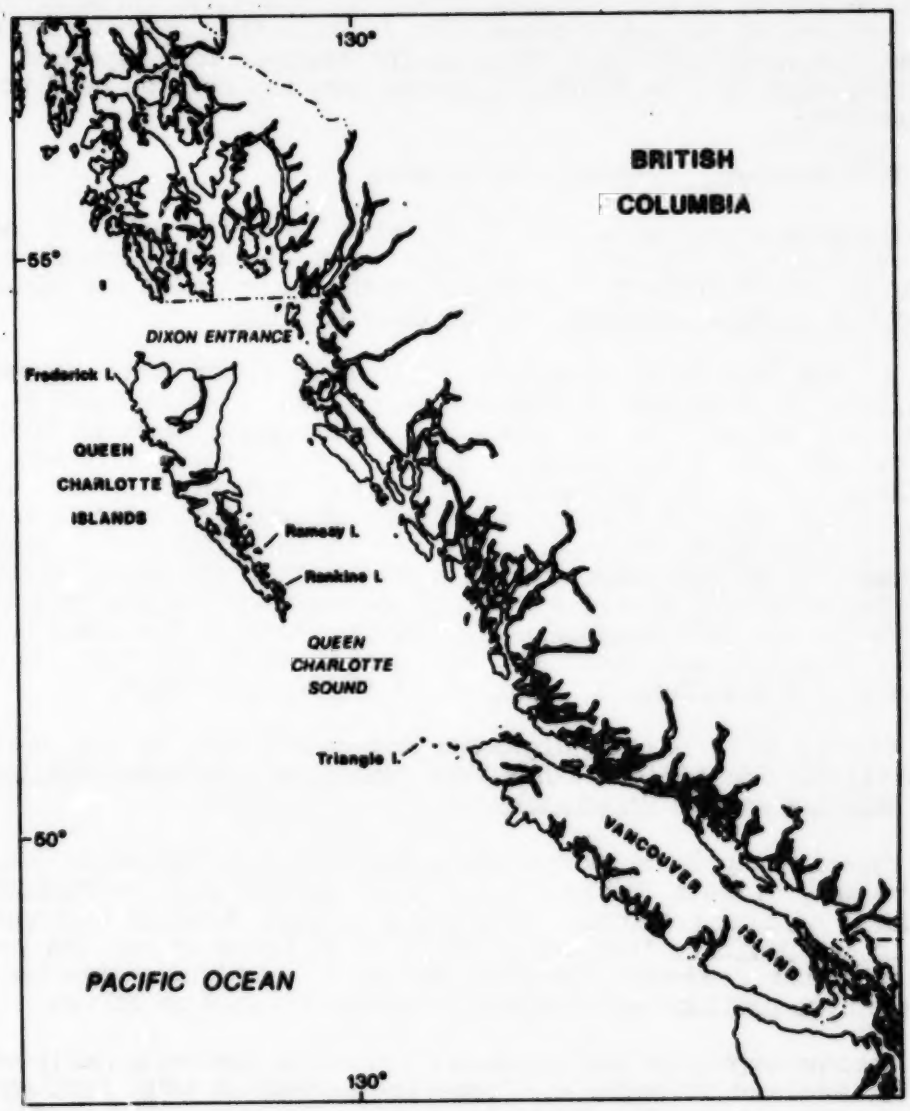

Figure 2. Location of nesting colonies of Cassin's Auklets where food samples were collected.

B. Food categories: occurrence and biomass

Nine food categories and unidentified digested matter were encountered in the nestling diet of Cassin's Auklets (Table 5). Calanoid copepods, euphausiids, fishes, carideans and hyperiid amphipods occurred most frequently in meal samples (Table 5). The first three categories made up most of the prey biomass (Fig. 3, Table 6). On Frederick Island, calanoid copepods and fishes were, on the average, more important in the nestling diet than on Triangle Island, but the reverse held true for euphausiids.

C. Prey species: occurrence and biomass

Neocalanus cristatus made up at least 99% of the calanoid copepods and was the most important food species of nestling Cassin's Auklets (Table 6). Other copepods encountered in the auklet meals were Neocalanus plumchrus, Calanus pacificus, and Metridia pacifica.

By far the most important euphausiid foods were Thysanoessa spinifera, T. longipes and Euphausia pacifica (Tables 7 and 8). Both adults and juveniles of the first two species were important food items for the auklets. Most Euphausia pacifica encountered were adults. T. spinifera was an important part of the birds' diet in all years, while T. longipes was identified as the principal euphausiid on Triangle Island in 1981 and 1982 and on Frederick Island in 1981 (Table 8). Euphausia pacifica was of some importance as a prey on Triangle Island in 1981 and 1982 (Table 8). Occasional euphausiid species found in the meal samples were T. raschii and Nematocelis difficilis. Many of the euphausids were partly digested and could not be identified to species, but were presumably T. spinifera, T. longipes and Euphausia pacifica.

Fishes were partly digested and could only occasionally be identified. Identified fishes were Ammodytes hexapterus, Hemilepidotus sp., Sebastes sp. and Hexagrammos sp.

Hyperiid amphipods and carideans did not constitute major components of the prey biomass (Table 6), but some species such as Parathemisto pacifica, Vibilia propingua, Pandalopsis dispar, Pandalus platyceros and Pasiphaea pacifica frequently occurred as foods in certain years on Triangle and Frederick Islands (Table 9). Of these species, only Parathemisto pacifica was observed on Ramsay and Rankine islands.

Besides amphipods and carideans, brachyuran larvae commonly occurred in bird meals on Triangle and Frederick islands in 1980, 1981 and 1982. The gooseneck barnacle, Pollicipes polymerus as well as unidentified squid, octopus and scyphozoid medusae were occasional prey on Triangle and Frederick islands.

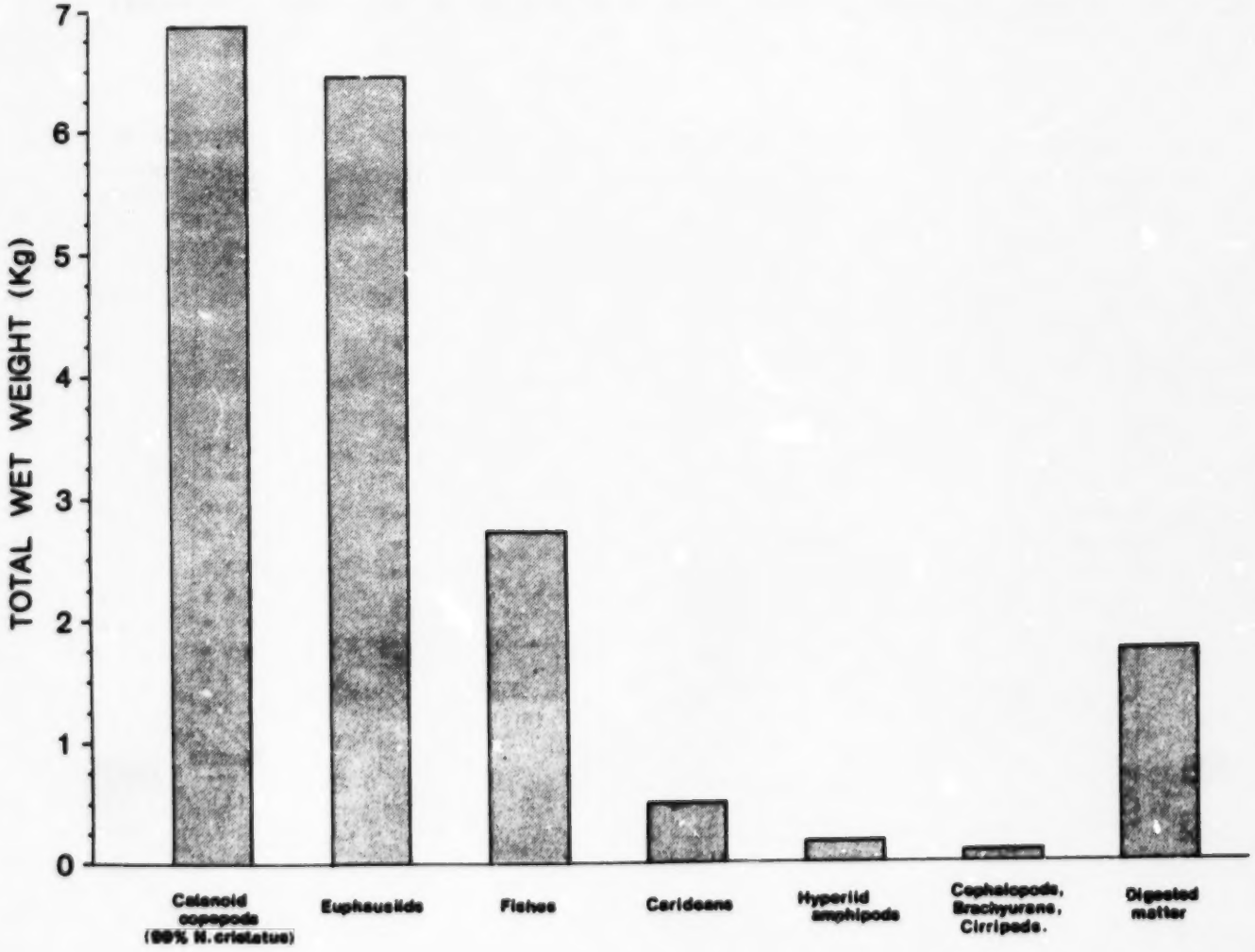

Figure 3. Overall composition of biomass (wet weight, 19 kg) of 998 meals of Cassin's Auklets, collected on Triangle, Frederick, Ramsay and Rankine islands from late May through July, 1978-1982.

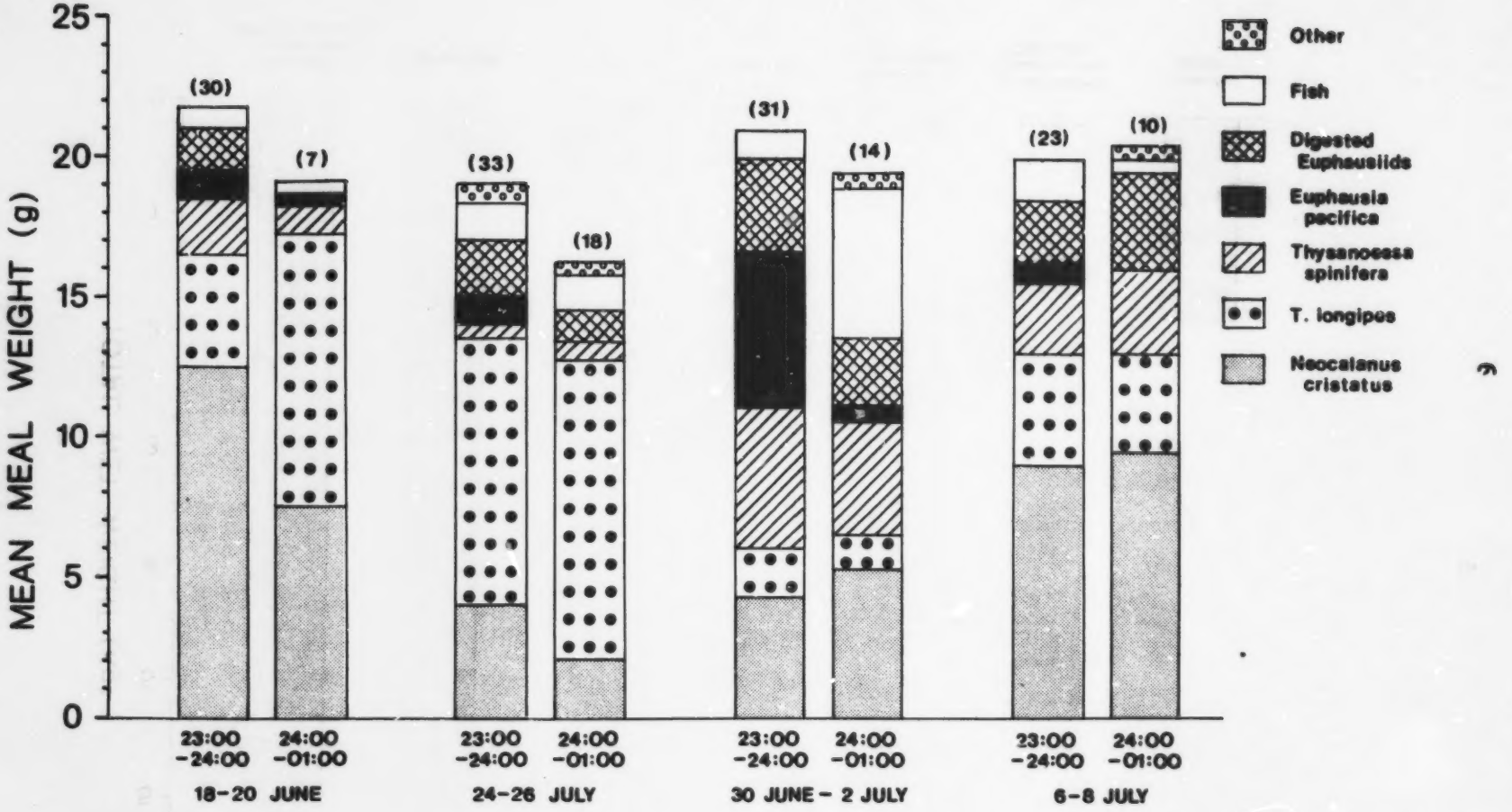

Figure 4. Comparison of average meal composition of nestling Cassin's Auklets between 23:00-24:00 h and 24:00-01:00 h on Triangle Island (number of meals in parentheses).

D. Changes in food composition

The mean composition of prey biomass in meals of nestling Cassin's Auklets at 4-day intervals on Triangle Island in 1982 is shown in Fig. 4. The same major prey categories occurred at all sampling periods (Fig. 4), but the composition of their occurrence changed significantly over the sampling period (Table 10). Similar seasonal changes in the diet of nestling Cassin's Auklets were previously observed by Vermeer (1981, 1985).

Neocalanus cristatus and Euphausia pacifica occurred significantly less in the second than in the first sampling hour at night, but the reverse held true for fishes (Table 11). Perhaps this reflects that auklets, which arrive at the colony after midnight, feed more on fishes which migrate to the sea surfce at dusk, than birds which arrive earlier.

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Table 1. Number of meals (n) and zooplankton biomass (g) collected from Cassin's Auklets on Triangle and Frederick islands from late May through July, 1978 to 1981, and from 1980 to 1981 respectively.

Collection period	Triangle Island								Frederick Island			
	1978		1979		1980		1981		1980		1981	
	n	g	n	g	n	g	n	g	n	g	n	g
27 May-3 June	28	526	39	869	44	671	34	624	32	495	6	95
12-17 July	-	-	-	-	-	-	-	-	42	662	18	281
25 June-4 July	42	757	46	1015	42	895	41	930	40	709	38	857
13-20 July	37	603	36	569	42	889	34	664	29	531	11	174
21-30 July	5	89	8	88	10	150	12	186	15	261	6	88
Total	112	1975	129	2541	138	2605	121	2404	158	2658	79	1495

Table 2. Number of meals (n) and zooplankton biomass (g) collected from Cassin's Auklets on Triangle, Ramsay and Rankine islands, May to July, 1982.

Collection periods	Triangle Island		Ramsay Island		Rankine Islands	
	n	g	n	g	n	g
30 May-3 June	-	-	27	455	23	470
18 June-20 June	37	783	-	-	-	-
24 June-26 June	51	960	-	-	-	-
30 June-2 July	45	1006	-	-	-	-
6 July-8 July	33	656	-	-	-	-
12 July-14 July	16	374	-	-	-	-
18 July-20 July	15	375	-	-	-	-
24 July-28 July	14	312	-	-	-	-
Total	211	4466	27	455	23	470

Table 3. Mean weights (in grams and SD) of meals carried by Cassin's Auklets to their nestlings on Triangle and Frederick islands, 1978 to 1981, and 1980 to 1981 respectively. Sample sizes are the same as in Table 1.

	Triangle Island				Frederick Island	
	1978	1979	1980	1981	1980	1981
27 May–3 June	18.8±10.2	22.3±7.9	15.3±7.2	18.4±9.3	15.5±7.8	15.8±9.0
12–17 June	-	-	-	-	15.8±7.9	15.6±8.6
25 June–4 July	18.0±6.9	22.1±7.8	21.3±8.8	22.7±8.7	17.7±8.6	22.6±8.3
13–20 July	16.3±7.3	15.8±7.3	21.2±8.0	19.5±8.6	18.3±8.3	15.8±6.3
21–30 July	17.8±6.6	11.0±8.5	15.0±9.3	15.5±9.4	17.4±9.0	14.7±6.6
Average meal size	17.6±8.0	19.7±8.5	18.9±8.5	19.7±9.3	16.8±8.3	18.9±8.4

Table 4. Mean weights (in grams and SD) of meals carried by Cassin's Auklets to their nestlings on Triangle, Ramsay and Rankine islands, 1982. Sample sizes are the same as in Table 2.

Collection periods	Triangle Island	Ramsay Island	Rankine Island
30 May–3 June	-	16.9±8.5	20.4±8.4
18 June–20 June	21.2±9.0		
24 June–26 June	18.8±9.5		
30 June–2 July	22.4±8.9		
6 July–8 July	19.9±9.4		
12 July–20 July	25.1±9.8		
24 July–28 July	22.3±7.9		
Average meal size	21.2±9.0	16.9±8.5	20.4±8.4

Table 5. Comparison of percentage occurrence of Cassin's Auklet prey, 1978-1982.

Major prey categories	Triangle Island					Frederick Island		Ramsay and Rankine islands
	1978	1979	1980	1981	1982	1980	1981	1982
Calanoid copepods (99% *Neocalanus cristatus*)	86.6	76.6	80.5	67.9	73.8	90.6	96.5	69.2
Euphausiids	73.2	57.4	83.9	80.9	93.5	65.6	94.2	100.0
Fishes	23.2	64.3	37.6	51.1	28.0	45.6	72.1	30.8
Carideans	22.3	25.6	23.5	9.9	13.6	58.3	31.4	42.3
Hyperiid amphipods	42.0	15.5	49.0	24.4	13.1	31.7	23.3	19.2
Cephalopods	-	-	0.7	7.6	0.9	0.6	10.5	-
Brachyurans (larvae)	-	-	16.1	9.9	8.4	2.8	5.8	7.7
Cirripeds (*Polymerus pollicipes*)	-	1.6	-	1.5	0.9	-	-	-
Scyphozoa (medusae)	-	-	-	1.5	1.4	-	2.3	1.9
Digested matter	89.3	70.5	72.5	-	2.3	5.6	-	7.8

Table 6. Comparison of average percentage wet weight of Cassin's Auklet prey, 1978-1982.

Major prey categories	Triangle Island						Frederick Island			Ramsay and Rankine islands
	1978	1979	1980	1981	1982	1978-82	1980	1981	1980-81	1982
Calanoid copepods (99% *Neocalanus cristatus*)	38.3	38.6	30.8	27.4	32.0	33.4	49.7	43.4	46.6	30.0
Euphausiids	24.8	15.0	25.3	39.6	58.4	32.6	15.4	31.8	23.6	51.4
Fishes	3.1	17.2	4.3	30.6	7.3	12.5	23.4	22.8	23.1	8.8
Carideans	3.3	5.0	0.7	0.1	1.4	2.1	7.7	0.7	4.2	1.0
Hyperiid amphipods	4.9	0.5	0.7	0.8	0.1	1.4	0.6	0.5	0.5	1.0
Cephalopods	-	-	0.01	1.2	0.01	0.3	0.8	0.4	0.6	-
Brachyurans (larvae)	-	-	0.2	0.3	0.1	0.1	0.01	0.3	0.2	1.5
Cirripeds (*Balymarus pollicipes*)	-	0.4	0.01	-	0.01	0.02	-	-	-	-
Scyphozoa (medusae)	-	-	-	0.02	0.02	0.01	-	0.05	0.03	trace
Digested matter	26.5	23.6	38.0	-	0.7	17.7	2.4	-	1.2	6.3

Table 7. Comparison of percentage occurrence of euphausiid prey of Cassin's Auklets, 1978-1982.

Prey species	Triangle Island					Frederick Island		Ramsay and Rankine Islands
	1978	1979	1980	1981	1982	1980	1981	1982
Thysanoessa spinifera (adults)	28.5	16.2	59.1	50.4	32.7	24.4	23.3	94.2
Thysanoessa spinifera (juveniles)*	-	-	4.7	15.3	25.2	10.0	7.0	28.8
Thysanoessa longipes (adults)	1.8	-	5.4	37.4	18.2	21.1	48.8	-
Thysanoessa longipes (juveniles)*	-	-	6.7	24.4	56.1	12.2	75.6	-
Thysanoessa raschii	0.9	3.9	-	-	-	-	-	-
Nematocelis difficilis	-	0.1	-	-	-	-	-	-
Unidentified Thysanoessa	10.7	8.5	-	-	-	-	-	-
Euphausia pacifica	13.4	1.6	21.5	23.7	18.7	18.3	5.8	9.6
Digested and unidentified euphausiids	68.8	38.0	40.9	13.0	15.4	30.0	4.7	3.8

* Not identified in 1978 and 1979.

Table 8. Comparison of percentage of wet weight of euphausiid prey of Cassin's Auklets, 1978-1982.

Major prey categories	Triangle Island					Frederick Island		Ramsay and Rankine Islands
	1978	1979	1980	1981	1982	1980	1981	1982
Thysanoessa spinifera (adults)	5.7	4.6	16.5	16.7	9.6	2.6	4.4	47.5
Thysanoessa spinifera (juveniles)	-	-	0.6	1.1	6.2	0.2	0.9	2.7
Thysanoessa longipes (adults)	0.5	-	0.5	5.8	4.3	1.6	4.2	-
Thysanoessa longipes (juveniles)	-	-	0.9	5.6	21.5	0.5	20.1	-
Thysanoessa raschii	0.1	0.2	-	-	-	-	-	-
Unidentified Thysanoessa	1.6	2.0	-	-	-	-	-	-
Euphausia pacifica	2.4	0.1	2.6	6.5	6.6	3.0	0.7	1.1
Digested and unidentified euphausiids	14.5	8.1	4.2	3.9	10.2	7.4	1.6	0.1

Table 9. Comparison of percentage occurrence of hyperiid amphipods and caridean prey of Cassin's Auklets, 1978-1982.

Major prey categories	Triangle Island					Frederick Island		Ramsay and Rankine islands
	1978	1979	1980	1981	1982	1980	1981	1982
Hyperiid amphipods								
Parathemisto pacifica (adults)	26.8	8.5	23.5	9.2	3.3	16.1	9.3	17.3
Parathemisto pacifica (juveniles)*	-	-	-	8.4	-	7.2	5.8	3.8
Vibilia propingua	29.5	0.8	22.8	-	-	12.2	2.3	-
Primno macropa	-	-	4.7	9.2	8.9	12.2	11.6	5.8
Hyperia medusarum	2.7	2.3	1.3	-	1.9	2.8	-	1.9
Hyperoche medusarum	1.8	-	-	5.3	0.9	-	2.3	-
Phronima sedentaria	0.9	-	-	-	-	1.7	-	-
Paraphronima sp.	-	-	-	-	0.5	-	-	1.9
Callipius sp.	-	1.6	-	-	-	-	-	-
Euphidippa sp.	-	1.6	-	-	-	-	-	-
Brachycelus sp.	-	-	6.7	-	-	2.2	-	-
Unid. and fragm. amphipods	7.1	7.8	8.1	-	-	-	-	-
Total hyperiid amphipods	42.0	15.5	49.0	24.4	13.1	31.7	23.3	19.2
Crideans								
Pandalopsis dispar	-	-	20.8	6.9	-	50.6	10.5	-
Pandalus platyceros	-	-	-	2.3	13.7	5.6	14.0	42.3
Eualus pacifica	22.3	25.6	0.7	-	-	0.6	-	-
Unid. and fragm. crideans				0.7	-	2.8	4.7	-
Total crideans	22.3	25.6	20.8	9.3	13.7	58.3	31.4	42.3

* Not identified in 1978 and 1979.

Table 10. Percentage occurrence of major prey items in meals of Cassin's Auklets during 3-day periods at 4-day intervals, Triangle Island, 1982. (Number of meals in parentheses.)

Major prey	Percentage occurrence			
	18-20 June (37)	24-26 June (51)	30 June -2 July (45)	6-8 July (33)
Neocalanus cristatus	86.5	66.7*	82.2	84.8
Thysanoessa spinifera	35.1	11.8*	48.9*	54.5
Thysanoessa longipes	67.6	70.6	42.2*	54.5
Euphausia pacifica	8.1	3.9	46.7*	9.1*
Fishes	18.9	15.7	35.6*	24.2

* Significantly different from preceding percentage occurrence ($p<0.05$).

Table 11. Percentage occurrence of major prey items in meals of Cassin's Auklets arriving at 23:00-24:00 h and at 24:00-1:00 h (Daylight Saving Time) at the Triangle Island colony, 18 June to 8 July 1982 (number of meals in parentheses).

Major prey	Percentage occurrence	
	23:00-24:00 h (117)	24:00-1:00h (49)
Neocalanus cristatus	81.2	73.5*
Thysanoessa spinifera	39.3	26.5
Thysanoessa longipes	59.0	59.2
Euphausia pacifica	22.2	6.1*
Fishes	20.5	30.6*

* Significantly different from preceding percentage occurrence ($p<0.05$).